AD 698 546

PETROLEUM PRODUCTS, PROPERTIES, QUALITY, APPLICATION

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22 August 1969

FTD-HT-23-347-68 Part 2 of 4

AD698546

FOREIGN TECHNOLOGY DIVISION

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FTD-HT-23-347-68
Part 2 of 4

EDITED TRANSLATION

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Source: Nefteprodukty, Svoystva, Kachestvo, Primeneniya, (Petroleum Products, Properties. Quality, Application) 1966, pp. 1-776

English Pages: 225 - 460

Translated Under: F33657-68-D-0865

PREPARED BY:

TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
WP-AFB, OHIO.

Chapter 4

BOILER FUELS

1. ADVANTAGES OF LIQUID FUELS AND THEIR CLASSIFICATION

Liquid boiler fuel, which represents the heavy residues of direct distillation and cracking residues (mazouts), together with thermal-refining products of coals and bituminous shales (oils and tars), is used in the boilers of marine and stationary boiler systems and for technical purposes (in smelting of steel, in thermal, heating and other industrial furnaces). Heavy crude petroleums lacking the light fractions are sometimes used as boiler fuels.

Liquid fuels have certain advantages over solid fuels:

1) high heat of combustion and high combustion rates, which make it possible to burn liquid fuel at high utilization of the firebox space, which may reach 1,500,000 kcal/(m^3·h) and more as compared to 350,000 kcal/(m^3·h) with solid fuels;

2) thorough combustion at comparatively small excess-air ratios;

3) low ballast content (ash, moisture);

4) possibility of automating supply of fuel to firebox;

5) simplicity of loading at points of production, shipment and unloading at customer's premises, as well as convenience of warehouse storage;

6) precision and simplicity of regulating boiler-system conditions.

Use of liquid fuels on ships makes it possible:

1) to increase the range of the ship with a given bunker weight capacity as compared with the use of solid fuel;

2) loading fuel between decks, thereby increasing the ship's useful hold capacity and improving its livability;

3) improve the maneuverability of the ships by means of higher boiler tuning and the possibility of emptying and rebunkering fuel tanks with comparative speed;

4) mechanize the fuel-burning process and accelerate firing and shutdown of the boilers.

TABLE 4.1

Classification of Boiler Fuels (Mazouts)

By origin	By sulfur content	By range of application	By nature of raw material	By production method
1. Petroleum — residual products of petroleum refining 2. Shale — neutralized shale tars (shale oil), obtained in the process of semicoking of shales in internally heated furnaces 3. Coal — residues from distillation of tars obtained from coking of coals	1. Low-sulfur: sulfur content not exceeding 0.5% 2. Sulfur-containing: sulfur content up to 2% 3. High-sulfur: sulfur content up to 3.5%	1. Fleet mazout — a higher-quality product of petroleum origin. Intended for burning in boilers of ships and vessels of the navy and river fleets. 2. Firebox mazout — fuel oil, heavy petroleums, Ukhta boiler fuel, shale and coal mazouts. Used in stationary boilers, industrial furnaces and in boilers of ocean-going and river vessels. 3. Fuel for open-hearth furnaces — a product of petroleum origin. 4. Export mazout — a product of petroleum origin. For export	Mazout of petroleum origin — low-paraffin and high-paraffin, gummy and high-gum. Coal mazout — coal and lignite types	Mazout of petroleum origin — straight-run petroleum mazout and cracking mazouts. Shale mazout — tunnel, chamber, generator. Coal mazout — semicoking, coking and gasification

Industrial furnaces operating on liquid fuel are smaller and simpler in construction than furnaces that use solid fuel, other conditions the same. The elimination of coal-stoking and ash-removal operations facilitates servicing. Further, the operational costs involved in the transport and burning of liquid fuels are lower than those for solid fuels.

Since mazouts are the principal liquid boiler fuels, all liquid fuels used in the fireboxes of boilers and furnaces are also called mazouts.

Mazouts can be classified [1, 2] on the basis of origin (petroleum, shale, coal), sulfur content (low-sulfur, sulfur-containing, high-sulfur) and range of application (fleet, firebox, open-hearth). The manufacturers classify mazouts on the basis of the type of raw material and the production technology (Table 4.1). Mazouts are also classified on the basis of density (light, heavy, superheavy) and viscosity (low-viscosity, medium-viscosity, high- and super-viscosity).

Heavy cracking residues (cracking mazouts) are the principal types used in the USSR's economy. Low-viscosity mazouts, especially straight-run types, are used only on oceangoing vessels and for special purposes. The super-viscosity cracking residues produced at the present time can be used directly as fuels for thermal electric power stations and in industrial boiler plants located near petroleum refineries. After dilution with low-viscosity components (solar oil, etc.) to obtain the viscosity specified by the standards for petroleum fuel [3], they can be shipped to other consumers.

Shale and coal mazouts are usually regarded as substitutes for mazouts of petroleum origin. Various tars and oils obtained in the refining of solid, liquid and gaseous fuels may also be used as substitutes.

2. PRODUCT CLASSES AND QUALITY OF COMMERCIAL BOILER FUELS PRODUCED IN THE USSR

At the present time, the industry is producing the following grades of liquid boiler fuels: 1) petroleum (mazout); 2) Ukhta; 3) high-paraffin petroleum; 4) export mazout; 5) coal and shale fuel mazouts (shale oil) [4].

Fuel oil mazout (AUSS 10585-63) is made in six grades: F5 and F12 fleet mazouts, Nos. 40, 100 and 200 firebox mazouts and OH (МП — МАРТЕНОВСКАЯ ПЕЧЬ) fuel for open-hearth furnaces. The grades of the mazouts are determined by the maximum permissible viscosity at 50°C in °VC [viscosity, conventional](°ВУ) (prior to 1965, fleet mazout was produced in three grades according to AUSS 1626-57: FS5, F12 and F20, and firebox mazout in six grades according to AUSS 1501-57: Nos. 20, 40, 60, 80, 100 and 200).

Fleet mazouts F5 and F12 are intended for burning in the boiler plants of ocean-going vessels. They can be used in internal-combustion engines and gas turbines. F12 mazout is a mixture of refinery products of low-sulfur petroleums: 60-70% straight-run

TAI . 4.2

Basic Quality Indices for Mazouts and OH Fuel (All-Union State Standard [AUSS] (ГОСТ) 10585-63)

1 Показатели	2 Мазуты флотские		4 Мазуты топочные			5 Топливо МП (для мартеновских печей)
	3 Ф5	Ф12	40	100	200	
6 Плотность при 20° С, г/см³, не более	—	—	—	1,015	—	1,015
7 Вязкость условная, °ВУ, не более:						
8 при 50° С	5,0	12,0	—	—	—	—
» 80° С	—	—	8,0	15,5	—	8,0—16,0
» 100° С	—	—	—	—	6,5—9,5	—
9 Вязкость динамическая, пз, не более:						
8 при 10° С	17,0	—	—	—	—	—
» 0° С	27,0	—	—	—	—	—
10 Температура вспышки, °С, не ниже:						
11 в закрытом тигле	80	90	—	—	—	—
12 в открытом тигле	—	—	90	110	140	110
13 Температура застывания, °С, не выше	—5	—8	+10	+25	+36	+25
14 Температура застывания топлив из высокопарафинистых нефтей, °С	—	—	+25	+42	+42	—
15 Теплота сгорания (низшая на сухое топливо), 16 ккал/кг (небраковочная):	9870	9870	—	—	—	9650
17 для малосернистых и сернистых топлив	—	—	9700	9650	9600	
18 для высокосернистых топлив	—	—	9550	9500	9450	
19 Зольность, %, не более	0,1	0,1	0,15	0,15	0,3	0,3
20 Механические примеси, %, не более	0,1	0,15	1,0	2,5	2,5	2,5
21 Вода, %, не более	1,0	1,0	2,0*	2,0*	23 1,0	2,0
22 Сера, %, не более	2,0	0,8	0,5 (для малосернистого) 2,0 (для сернистого) 24 3,5 (для высокосернистого) 25			0,5
26 Смолистые вещества, %, не более	50	50	—	—	—	—
27 Коксуемость, мал. %, не менее	—	—	—	—	—	12

*Up to 5% is permitted for mazouts that have been shipped by water or poured under live-steam heating.

1) Indicator
2) Fleet mazouts
3) F5
4) Firebox mazouts
5) OH fuel (for open-hearth furnaces)
6) Density at 20°C, g/cm³, not above
7) Conventional viscosity, °VC, not above:
8) At
9) Dynamic viscosity, poise, not above:
10) Flash point, °C, not below
11) In closed crucible
12) In open crucible
13) Pour point, °C, not above
14) Pour point of fuels from high-paraffin petroleums, °C
15) Heat of combustion (low, for dry fuel)
16) kcal/kg (acceptance minimum):
17) For low-sulfur and sulfur fuels

18) For high-sulfur fuels
19) Ash, %, not above
20) Mechanical impurities, %, not above
21) Water, %, not above
22) Sulfur, %, not above
23) (for low-sulfur fuels)
24) (for sulfur-containing fuels)
25) (for high-sulfur fuels)
26) Gummy substances, %, not above
27) Coking capacity, % by mass, not below.

mazout, 10-12% gas-oil fractions (black solar oil), and 20-30% cracking residue. The proportions of the components are not constant, and depend on the grade of mazout to be made and the quality of the components. Mazout F5 consists of straight-run sulfur-petroleum products: 60-70% mazout, 30-40% gas-oil fractions. It may contain up to 22% kerosene-gas-oil fractions from thermal and catalytic cracking. The viscosity specified for F5 sulfur-containing mazout (dynamic viscosity in poises) at 10 and 0°C is determined on M.P. Volarovich's rotary viscosimeter. By agreement with the consumer, no less than 0.2% of VNII NP-102 or VNII NP-103 additive is used in fuel for marine boilers.

Firebox mazouts are heavy cracking residues, either alone or mixed with straight-run mazouts. Asphalt is sometimes introduced in the production of high-viscosity mazouts. In addition to high viscosity and a positive pour point, they are allowed higher contents of mechanical impurities, sulfur, and water and lower heats of combustion than fleet mazouts. Because of the high viscosity of firebox mazouts at 50°C and the difficulty of determining it, viscosity is defined and standardized: at 80°C for Nos. 40 and 100 mazouts and at 100°C for No. 200 mazout. Firebox mazouts are intended for burning in ship boiler plants (mazout 40), stationary boiler rooms and industrial furnaces.

The grade of the mazouts used for stationary boilers is specified as a function of nozzle throughput, stoking equipment, and whether the installations are provided with preheaters. Heavy boiler mazouts are used in stationary boilers with high-capacity preheating and high-throughput nozzles.

For moderate sized industrial furnaces with small nozzles using up to 25-50 kg of fuel per hour, light boiler fuel is recommended; a medium-viscosity fuel such as No. 40 mazout is necessary for nozzles handling 50-100 kg/hour, and high-viscosity mazouts such as No. 100 or with even higher viscosity should be used for nozzles with flow rates above 100 kg/hour and a preheating system [1].

Open-hearth OH fuel is obtained from low-sulfur raw materials. Its quality indices resemble those of No. 100 firebox mazout. Coking capacity, which is also standardized for it, is determined after removal of mechanical impurities.

The quality indices of fleet and firebox mazouts and MP fuel are listed in Table 4.2.

Fuel oils include residues from distillation of Ukhta petro-

TABLE 4.3

Quality Indices of Fuel Oils from Ukhta and West Ukrainian Petroleums

1 Показатели	2 Ухтинское котельное топливо	3 Топливо котельное нефтяное (УРВТУ-59)
4 Вязкость условная, °ВУ, не более:		
5 при 75° С	30	—
» 80° С	—	1,0—2,5
6 Температура, °С:		
7 вспышки (в открытом тигле), °С, не ниже	110	95
8 застывания, °С, не выше	+25	+42
9 Теплота сгорания (низшая на сухое топливо), ккал/кг (небраковочная)	—	9870
10 Зольность, %, не более	0,50	0,20
11 Сера, %, не более:		
12 в малосернистом топливе	1,4	0,5
13 в сернистом топливе	—	1,0
14 Вода, %, не более	2,0	2,0

1) Index
2) Ukhta boiler fuel
3) Petroleum boiler fuel (URVTU-59)
4) Conventional viscosity, °VC, not above
5) At
6) Temperatures, °C
7) Flash point (open crucible), °C, not below
8) Pour point, °C, not above
9) Heat of combustion (low, dry fuel), kcal/kg (minimum acceptance)
10) Ash, %, not above
11) Sulfur, %, not above
12) In low-sulfur fuel
13) In sulfur-containing fuel
14) Water, %, not above.

TABLE 4.4

Principal Quality Indices of Export Mazouts (ETS 638-57)

1 Показатели	2 Марки мазутов		
	+10	0	−5
3 Плотность ρ_4^{20}, не более	0,990	0,980	0,965
4 Вязкость условная, °ВУ, при 50° С, не более	30	40	12
5 Температура, °С:			
6 вспышки (в закрытом тигле), °С, не ниже	65	80	78
7 застывания, °С, не выше	+10	0	−5
8 Теплота сгорания (низшая на сухое топливо), ккал/кг, не менее	9800	9800	9800
9 Зольность, %, не более	0,3	0,3	0,3
10 Сера, %, не более	2,5	2,5	2,5
11 Вода и механические примеси, %, не более	2,0	2,0	2,0

1) Index 2) Mazout grades
3) Density ρ_4^{20}, not above
4) Conventional viscosity, °VC, at 50°C, not above
5) Temperatures, °C

6) Flash point (open crucible), °C, not below
7) Pour point, °C, not above
8) Heat of combustion (low, dry fuel), kcal/kg, not below
9) Ash, %, not above
10) Sulfur, %, not above
11) Water and mechanical impurities, %, not above.

TABLE 4.5

Principal Quality Indices of Coal and Shale Mazouts

A Показатели	B Мазут-топливо угольный (ТУ 464—53)		C Сланцевое масло—мазут (ГОСТ 4806—49)	D Дистиллятный мазут из сланцевой смолы [5]
	1	2		
E Вязкость условная, при 75° C, °ВУ, не более	5	3	3,5	F При 50° C 6,58
G Температура, °C:				
H вспышки (в открытом тигле), не ниже	100	70	65	I 115 (в закрытом тигле)
J застывание, не выше	+25	+5	−5	−17
K Теплота сгорания, ккал/кг	—	—	—	8820
L Смолистые вещества, %	—	—	—	60
M Зольность, %, не более	0,3	0,3	0,3	0,04
N Сера, %, не более	0,5	0,5	2,0	0,55
O Вода, %, не более	2,0	2,0	5,0	P Отсутствие

A) Index
B) Coal fuel mazout (TS 464-53 [technical spec. (ТУ)
C) Shale oil mazout (AUSS 4806-49)
D) Distillate mazout from shale tar [5]
E) Conventional viscosity, at 75°C, °VC, not above
F) At
G) Temperatures, °C
H) Flash point (in open crucible), not below
I) (in closed crucible)
J) Pour point, not above
K) heat of combustion, kcal/kg
L) Gummy substances, %
M) Ash, %, not above
N) Sulfur, %, not above
O) Water, %, not above
P) None.

leums (Ukhta boiler fuel) and high-paraffin petroleums from the West Ukrainian deposits (UR VTU-59 boiler fuel oil). The quality indices of these fuels are given in Table 4.3.

Ukhta fuel is intended for burning in large boiler plants, and high-paraffin mazout in stationary boilers and industrial furnaces.

Export mazout (ETS 638-57 [ЭТУ]) is made in three grades: +10, 0, and -5. The mazouts are graded in accordance with pour point (Table 4.4).

Coal-fuel mazout (TS 464-53) is a residue from distillation of tars obtained in semicoking of coal. It is used in boiler installations and industrial furnaces (Table 4.5).

Shale oil (AUSS 4806-49) is neutralized shale tar obtained in thermal decomposition of kerogen (the organic matter of bituminous shales) in internally heated furnaces (tunnel, generator, chamber). As regards quality (see Table 4.5), shale mazout is similar to the fleet grade. However, shale oil is not used on ocean-going vessels because of its low heat of combustion and poor separation after mixing with water. The oil is so dense (1000 and more) that water that has gotten into it does not settle, but floats on it or is distributed nonuniformly throughout its entire mass in the form of pockets and separate layers.

TABLE 4.6

Physicochemical Properties of Liquid Products Recommended as Substitutes [6]

1 Жидкие продукты	2 Исходное сырье	3 Плотность ϱ_4^{20}	4 Вязкость условная °ВУ при температуре			5 Температура, °C			9 Теплота сгорания, ккал/кг	
			50° C	75° C	100° C	6 вспышки	7 воспламенения	8 застывания	10 горючая низшая	11 рабочая низшая
	12 Челябинский уголь	—	22,53	0,98	2,83	—	—	—	8350	8060
13 Смола	14 Каменный и кизеловский угли: сырье Губахинского коксохимического комбината	1,155	6,77	2,10	1,40	107	—	18	8334	8251
15 Пек	16 Кизеловский уголь Нижне-Тагильского коксохимического завода	—		17 ВУ$_{180}$ Не течет	18 ВУ$_{170}$ Течет по каплям	—	—	—	8640	8610
19 Нейтральное масло	20 Нижне-Тагильского торфохимического завода	0,917 21 (при 15° C)	1,63	1,22	1,08	67	89	21	9624	9363
22 Парафиновое масло	20 Нижне-Тагильского торфохимического завода	0,971	1,67	1,38	1,28	75	93	7	8832	8737
13 Смола	23 Нижне-Тагильского коксохимического завода	1,159	24 Не течет	27,0	6,37	139	—	5	8412	7135

1) Liquid product
2) Original raw material
3) Density
4) Conventional viscosity, °VC, at temperature of
5) Temperatures, °C
6) Flash point
7) Ignition point
8) Pour point
9) Heat of combustion, kcal/kg
10) Fuel, low
11) Working, low
12) Chelyabinsk coal
13) Tar
14) Hard and Kizel coals; raw material of Gubakha coke and chemical combine
15) Pitch
16) Kizel coal of Nizhne-Tagil coke and chemical plant
17) VC_{180}. Does not flow

18) VC_{170}. Flows dropwise
19) Neutral oil
20) Nizhne-Tagil peat-chemical plant
21) At
22) Paraffin oil
23) Nizhne-Tagil coke and chemical plant
24) Does not flow.

Under semiindustrial conditions, a technology has been worked out for the production of distillate mazout – the 50% fraction in vacuum distillation of the tar residue boiling above 325°C [5]. Distillate mazout pours at low temperature and separates well from water (see Table 4.5).

A number of products are used as mazout substitutes (Table 4.6).

3. PRODUCT CLASSES AND QUALITY OF COMMERCIAL BOILER FUELS PRODUCED ABROAD [7]

In foreign countries, it is customary to classify boiler fuels as distillate (furnace) and residual (mazout) types.

Furnace fuels are medium distillate products obtained in thermal and catalytic cracking of petroleum products and in coking of residual fuels. They are used chiefly for heating buildings (to 60%), in railroad transportation, and in industry. Furnace fuels are sometimes called domestic fuels (England), light fuels (France), or nozzle fuels (USA). The grading of furnace fuels is a function of viscosity and the purpose of the fuel or the type of nozzle.

Mazouts are intended for burning in the fireboxes of transportation and stationary steam boilers, in various industrial furnaces, and for heating buildings. Mazouts are also used as fuels for slow diesels and gas-turbine engines.

Mazouts are classified by origin (petroleum, coal, shale), production technology (straight-run, cracking mazouts), purpose (firebox and bunker or domestic-communal, industrial and marine: special fleet and bunker grades) and physicochemical indices (density and viscosity). In the official specifications of a number of countries (Belgium, France, etc.) and also individual petroleum companies ("Regent," "Shell," "Esso," etc.), mazouts are classified on the basis of the above criteria as light, medium, heavy and even superheavy (Belgium). Depending on viscosity, they are classified as low-viscosity, medium-viscosity and high-viscosity (Federal Republic of Germany, etc.). In the specifications of a number of countries (USA, Japan, etc.), no such division is made; however, viscosity is also used as a basis for actual grading of mazouts.

For the most part, boiler-fuel quality is evaluated abroad on the basis of the same physicochemical indices as in the USSR. Only the methods of determining certain constants and their evaluation are different.

1. **Viscosity.** The viscosities of residual fuels are determined: in the USA in Saybolt universal (low-viscosity mazouts) and Saybolt-Furol (high-viscosity grades) viscosimeters; in England in Redwood viscosimeters; in Italy and other European countries, in the Engler viscosimeter.

Some specifications indicate simultaneously the kinematic viscosity in cst as obtained by conversion.

2. **Pour point.** A number of countries use a method similar to ASTMD 97-59 (USA) to determine the pour points of residual fuels after preheating of the fuel specimen to 46°C and cooling to 32.2°C. It also provides for determination of the so-called maximum pour point. In this case, the specimen is preheated to 104.4°C. The maximum pour point is also determined by the method of JVM 201-50. The fuel sample is heated to 100°C and cooled to -6.7°C. Then nine separate samples are heated to a given temperature (between 32.2 and 87.8°C), followed by determination of the pour point. The lowest pour point obtained in this process for the mazout is taken as the maximum pour point.

3. **Fluidity.** To establish a guideline temperature at which the mazout remains mobile and can be pumped through mazout lines, tests for fluidity by a method proposed by the Arabian-American Oil Company and incorporated into U.S. Navy Department Specification MIL-F-859D have been introduced.

Fluidity is determined at 0°C in a U-tube connected to a vacuum pump. The mazout is considered to have passed the test and retained mobility in operation at 0°C if some small motion of the mazout in the tube is observed after pumping for 30 min at a pressure not exceeding 0.2 atm.

4. **Thermal stability.** Thermal stability is an index to the tendency of a mazout to form deposits during storage and heating (carbenes, carboids, asphaltenes, tars, mechanical impurities, and water) such as make work with them difficult.

In the widely accepted ASTMD 1661-59T method, thermal stability is determined in a glass instrument in which the mazout, heated to 98°C, is circulated for 6 hours. Stability is established by comparing the external appearance of a steel bushing that is heated to 176°C and washed by the mazout with a reference bushing. When a coke-like film is present on the bushing (after washing with benzene), or it has darkened greatly, the mazout is considered to be unstable.

5. **Explosiveness.** In the USA (specification MIL-F-859D), explosiveness specifications have been applied to mazouts as a result of fuel-tank explosions that have occurred aboard ships due to accumulation of an explosive mixture above the surface of the oil during storage. The explosive mixture contains hydrogen sulfide, propane and other volatile hydrocarbons.

Explosiveness is determined with a device used to determine that of the gas-air mixture in petroleum storage tanks. A mazout passes the test if the explosiveness of vapors liberated when it

is heated to 51.6°C and shaken for 5 min is lower than that of the gas mixture (methane, ethane, propane) established during calibration of the device.

TABLE 4.7

US Specification ASTM D 396-60T for Boiler Fuels (Distillate and Residual)

1 Показатели	2 Сорта топлив				
	№ 1	№ 2	№ 4	№ 5	№ 6
3 Плотность при 15,6° С, т/м³ не выше	0,850	0,898	—	—	—
4 Вязкость кинематическая, сст:					
5 при 37,8° С, не более	2,2	3,6	26,4	—	—
6 не менее	1,4	2,0	5,8	32,1	—
5 при 50° С, не более	—	—	—	81	638
6 не менее	—	—	—	—	92
7 Вязкость условная, °ВУ:					
5 при 37,8° С, не более	1,12	1,25	3,73	—	—
6 не менее	1,04	1,10	1,46	4,47	—
5 при 50° С, не более	—	—	—	10,90	86,13
6 не менее	—	—	—	—	12,40
8 Температура, °С:					
9 вспышки (в закрытом тигле), не ниже	37,8	37,8	54,4	54,4	65,6
10 застывания, не выше	−17,8	−6,7	−6,7	—	—
Фракционный состав: 11					
12 10% перегоняется при температуре, °С, не выше	215,6	—	—	—	—
13 90% перегоняется при температуре, °С:					
14 не выше	287,8	337,8	—	—	—
15 не ниже	—	282	—	—	—
16 Коксуемость 10%-ного остатка по Конрадсону, % не более	0,15	0,35	—	—	—
17 Коррозия (проба на медную пластинку)	18 Выдерживает	—	—	—	—
19 Зольность, %, не более	—	—	0,10	0,10	—
Сера, %, не более 20	0,5	1,0	21 Не ограничено		
22 Содержание воды и нерастворимых осадков, объемн. %, не более	23 Следы	0,10	0,50	1,00	2,00

1) Index
2) Fuel grade
3) Density at 15.6°C, tons/m³, not above
4) Kinematic viscosity, cst
5) At ... °C, not above
6) Not below
7) Conventional viscosity, °VC
8) Temperatures, °C
9) Flash point (in closed crucible), not below
10) Pour point, not above
11) Fractional composition
12) 10% distilled over at temperature, °C, not above
13) 90% distilled over at temperature, °C
14) Not above
15) Not below

16) Coking capacity of 10% residue according to Conradson, %, not above
17) Corrosion (copper-plate test)
18) Passes
19) Ash, %, not above
20) Sulfur, %, not above
21) Not limited
22) Water and insoluble-residue content, % by volume, not above
23) Traces.

In the USA, the most commonly applied specification is ASTM D 396-60T, which provides for the production of five grades of boiler (nozzle) fuels of petroleum origin: Nos. 1, 2, 4, 5 and 6.

Grades Nos. 1 and 2 are distillate fuels (furnace type). Fuel No. 1 is intended for burning in installations with vaporizing nozzles, and fuel No. 2 in combined (vaporization and atomizer) installations. Fuel No. 4 is usually a mixture of medium-viscosity distillate fuel with residual fuel, but may also be residual. It is used in installations without preheating. Grades Nos. 5 and 6 are residual fuels (mazouts). Boiler installations equipped with fuel preheaters operate on these fuels. Mazout No. 6, as a higher-viscosity grade, is used in large boiler installations with powerful preheaters. The quality requirements for boiler fuels according to the specifications of ASTM 396-60T are given in Table 4.7.

Detailed characterizations of residual fuels of the various types produced in the USA are listed in Table 4.8.

Table 4.9 presents US Naval Specification MIL-F-859D for naval fuels. It establishes two mazout grades: special (fleet) and heavy. The special grade is intended for use in the steam-boiler fireboxes of naval vessels, and the heavy mazout for steam-boiler installations of government vessels and shoreline powerplants.

In England, the prevailing specification is that of the British Standards Institute (Table 4.10), which is extended to distillate and residual fuels obtained by refining petroleums and shales (BS 2869-57). Grade D is used for automatic nozzles in domestic and other similar installations; mazouts F, G and H are used in boiler installations fitted with preheaters. Mázout E is used without preheating.

As necessary, the requirements as to pour point and sulfur and ash contents are established by contract between the supplier and the customer. Owing to the absence of a number of indicators in Specification BS2869-57, individual company specifications are used extensively in England (Table 4.11).

In the Federal Republic of Germany, fuels from coals and lignites are used extensively in addition to petroleum fuels. According to the government specification DIN 51603 (Table 4.12), four fuel grades are distinguished: EL, L, M and S. Grades EL and L are of the distillate-fuel type, the quality of grade M resembles that of fleet mazout F5, and grade S resembled firebox mazout No. 60. The fuel obtained from coal and lignite, and especially grade EL,

TABLE 4.8

Quality of Typical Commercial Residual Fuels of the USA

1 Показатели	2 Сорта и типы топлив											
	№ 4				№ 5				№ 6			
	A	B	C	D	A	B	E	F	B	C	G	H
3 Плотность при 15,6° C, $m/м^3$	1,0078	0,9273	0,9402	0,9129	1,0143	0,9509	0,9516	0,9972	0,9732	0,9672	0,9659	0,9840
4 Вязкость условная, °ВУ:												
5 при 21° C	6	4,32	—	6,81	—	—	—	—	—	—	—	—
» 37,8° C	2,8	2,56	2,62	3,03	11,37	10,72	5,44	—	—	—	—	157
» 50° C	2,02	2,03	2,05	—	5,70	5,94	3,45	24,1	51,16	45,5	63,84	53,6
» 65° C	—	—	—	—	—	—	—	—	—	—	24,70	—
» 98,9° C	—	—	—	[illegible],25	1,60	1,70	1,50	2,96	4,93	4,65	5,74	5,20
6 Температура, °C:												
7 вспышки (в закрытом тигле)	115,6	104,4	84,4	154,4	118,3	118,3	98,9	123,9	121,1	112,8	193,3	121,1
8 вспышки (в открытом тигле)	123,9	115,6	96,1	157,2	137,8	137,8	115,6	143,3	148,9	121,1	210,0	140,6
9 воспламенения (в открытом тигле)	141,1	132,2	110,0	179,4	154,4	151,7	135,0	171,1	185,0	154,4	232,2	196,1
10 застывания	−31,7	−23,3	−37,2	−45,6	−20,6	−6,7	−48,3	−15,0	7,2	−15,0	10	15,5
11 Термическая стабильность, баллы	1	1	1	1	1	1	1	1	1	1	1	1
12 Взрываемость, %	5	5	15	0	5	4	14	14	45	12	5	14
13 Фракционный состав, °C:												
14 начало кипения	233,9	101,1	212,8	238,3	240,6	243,9	218,9	237,8	215,0	212,8	—	212,8
15 перегоняется при температуре, °C:												
5%	268,4	231,7	227,2	—	274,4	276,1	248,3	279,4	290,0	253,9	—	298,9
10%	276,7	270,6	241,7	315,6	288,9	290,6	260,1	301,7	337,7	283,3	—	350,0
20%	295,6	283,3	261,1	332,2	310,6	326,1	287,2	335,0	397,0	336,8	—	383,0
30%	311,1	295,6	279,4	342,8	333,3	350,0	303,9	372,0	446,1	391,8	—	410,5
40%	323,9	309,4	305,0	352,8	354,4	383,0	321,1	442,0	515,6	462,0	—	444,0
50%	339,4	322,8	333,3	362,8	383,0	423,9	346,1	496,0	537,4	507,8	—	494,0
60%	355,0	350,0	362,8	373,9	434,0	475,0	419,5	527,0	540,0	523,9	—	568,0
70%	383,0	402,0	403,0	386,0	485,6	537,8	506,0	538,0	559,0	529,0	—	—
80%	434,0	494,3	495,0	402,0	535,0	568,0	—	558,0	569,0	—	—	—
90%	490,5	540,0	537,8	422,0	560,0	—	—	—	—	—	—	—
16 конец кипения	540	92% 576	537,8	466	90% 560	80% 568	76% 529	89% 565	88% 566	72% 529,4	—	60% 568
17 Всего перегоняется, %	98	92	90	99	90	80	76	89	88	72	—	60
18 Содержание элементов, части на миллион:												
19 алюминий	0,6	4	4	—	4	20	5	4	40	10	1,5	30
20 кальций	0,3	3	2,8	—	2,5	1	4	5	3	7	[illegible]	4
21 медь	0,05	0,04	—	—	0,3	0,3	0,1	0,3	0,5	—	0,04	0,4
22 железо	4	1	1,2	—	15	10	8	20	40	3	0,6	5
23 магний	0,6	1	19	—	5	1	9	5	4	47	1	10
24 марганец	0,08	0,1	—	—	0,5	0,3	0,5	0,7	1	—	—	0,7
25 никель	0,2	—	8	—	10	10	20	10	20	20	12	20
26 калий	0,09	—	0,4	—	0,4	5	0,1	1	1	1	0,2	1
27 кремний	1	2	2,4	—	4,0	30	4	3	40	6	5,7	20
28 натрий	0,4	4	10	—	6,5	5	14	17	11	26	4,0	14
29 олово	0,3	0,3	—	—	1,5	0,4	—	—	—	—	—	0,3
30 свинец	1	0,9	—	—	10	3	2	3	9	—	0,4	8
31 ванадий	0,7	4	107	—	3,5	11	71	8	14	417	40	110
32 цинк	—	4	—	—	—	—	—	—	—	—	—	—
33 Содержание, %:												
34 воды и осадка, %	0,10	0,10	0,10	Следы	0,10	0,80	0,10	0,10	1,0	0,10	0,50	1,0
35 осадка (определяемого экстракцией), %	0,06	0,10	0,10	0,01	0,06	0,06	0,10	0,08	0,12	0,05	0,06	0,08
36 Вода (определяемая перегонкой), %	37 Следы				37 Следы				37 Следы			
38 Коксуемость по Конрадсону, остаток, %	5,58	6,68	4,30	6,10	7,22	6,62	5,76	8,15	10,2	10,7	8,8	11,5
39 Зольность, %	0,016	0,006	0,029	0,0001	0,009	0,013	0,025	0,035	0,022	0,073	0,010	0,040
40 Сера, %	0,56	0,57	1,90	0,22	0,50	0,60	1,90	0,60	0,78	2,36	3,86	3,07

1) Index
2) Grades and types of fuels
3) Density at 15.6°C, tons/m³
4) Conventional viscosity, °VC
5) At
6) Temperatures, °C
7) Flash point (in closed crucible)
8) Flash point (open crucible)
9) Ignition point (open crucible)
10) Pour point
11) Thermal stability, points
12) Explosiveness, %
13) Fractional composition, °C
14) Start of boiling
15) Distilled over at temperatures, °C
16) End point
17) Total distilled over, %
18) Content of elements, parts per million
19) Aluminum
20) Calcium
21) Copper
22) Iron
23) Magnesium
24) Manganese
25) Nickel
26) Potassium
27) Silicon
28) Sodium
29) Tin
30) Lead
31) Vanadium
32) Zinc
33) Contents, %
34) Water and sediment, %
35) Sediment (determined by extraction), %
36) Water (determined by distillation), %
37) Traces
38) Conradson coking capacity, residue, %
39) Ash, %
40) Sulfur, %.

TABLE 4.9

USA Specification MIL-F-859D for Boiler Fuels

1 Показатели	2 Мазут	
	3 Специальный	4 Тяжелый
5 Плотность при 15,6° С, не выше	0,9895	1,000
6 Вязкость условная, °ВУ:		
7 при 29,5° С, не менее	6,7	
8 » 50° С, не более	6,7	44
9 Температура, °С:		
10 вспышки (в закрытом тигле), не ниже	65,6	65,6
11 воспламенения, не ниже	93,3	93,3
12 застывания (максимальная), не выше	−9,4	10
13 Взрываемость, %, не более	50	50
14 Термическая стабильность	15 Выдерживает	
16 Коксуемость по Конрадсону, %, не более	0,15	—
17 Текучесть, °С, не выше	0	—
18 Содержание воды и нерастворимых осадков, объемн. %, не более	0,5	—
19 Механические примеси (определяемые экстракцией), %, не более	0,12	0,15
20 Вода (определяемая перегонкой), объемн. %, не более	0,5	0,5
21 Сера, %, не более	3,5	—
22 Зольность, %, не более	0,1	0,12

1) Index
2) Mazout
3) Special
4) Heavy
5) Density at 15.6°C, not above
6) Conventional viscosity, °VC
7) At 29.5°C, not below
8) At 50°C, not above

9) Temperatures, °C
10) Flash point (closed crucible), not below
11) Ignition point, not below
12) Pour point (maximum), not above
13) Explosiveness, %, not above
14) Thermal stability
15) Passes
16) Conradson coking capacity, %, not above
17) Fluidity, °C, not above
18) Content of water and insoluble residues, % by volume, not above
19) Mechanical impurities (determined by extraction), %, not above
20) Water (determined by distillation), % by volume, not above
21) Sulfur, %, not above
22) Ash, %, not above.

TABLE 4.10

Specification BS 2869-57 of British Standards Institute

1 Показатели	2 Топливо для отопления	3 Мазут для промышленных и морских топок			
	D	E	F	G	H
4 Вязкость кинематическая, *cст*:					
5 при 37,8° C, не выше	7,5	—	—	—	—
6 » 50 °C, не выше	—	36	125	370	690
7 Вязкость условная, °ВУ при 50° C	—	4,8	16,5	48,7	91,0
8 Температура вспышки (в закрытом тигле), °C, не ниже	54,4	65,6	65,6	65,6	65,6
9 Теплота сгорания, *ккал/кг*:					
10 высшая	10 300	10 200	10 100	10 000	9900
11 низшая	9700	9550	9480	9430	9380
12 Коксуемость по Конрадсону, %, не более	0,2	—	—	—	—
13 Зольность, %, не более	0,01	14 По требованию потребителей			
15 Сера, %, не более	2,0	16 То же			
17 Вода, объемн. %, не более	0,25	0,5	1,0	1,0	1,5

1) Index
2) Fuel for heating
3) Mazout for industrial and marine fireboxes
4) Kinematic viscosity, cst
5) At 37.8°C, not above
6) At 50°C, not above
7) Conventional viscosity, °VC at 50°C
8) Flash point (closed crucible), °C, not below
9) Heat of combustion, kcal/kg
10) High
11) Low
12) Conradson coking capacity, %, not above
13) Ash, %, not above
14) To customer's requirements

15) Sulfur, %, not above
16) Same
17) Water, % by volume, not above.

TABLE 4.11

Mazout Specifications Developed by Individual Companies in England (1960)

1 Показатели	2 Мазуты фирмы «Риджент»			6 Мазуты фирмы «Кифт Ойль Продактс»		
	3 легкий	4 средний	5 тяжелый	3 легкий	4 средний	5 тяжелый
7 Плотность при 15° С, $т/м^3$	0,930—0,950	0,950—0,970	0,960—0,980	0,930	0,950—0,980	0,990
8 Вязкость условная °ВУ при 50° С	3,2—4,2	8,8—13,0	31—42	3,2—4,2	8,8—13,0	35,5—42,0
9 Температура, °С:						
10 вспышки (в закрытом тигле), °С, не ниже	65,6	65,6	65,6	74,0	85,0	93,0
11 застывания, °С, не выше	—17,8	—1,1	+10	—1,0	—1,0	+10
12 Теплота сгорания высшая, ккал/кг, не менее	10 390	10 334	10 279	10 390	10 344	10 279
13 Зольность, %, не более	0,01	0,03	0,05	0,01	0,05	0,07
14 Сера, %	1,5—2,5	2,0—2,5	2,5—3,5	2,5	2,0—3,0	2,0—3,0
15 Механические примеси масс. %, не более	0,01	0,03	0,05	0,01	0,02	0,03
16 Вода, объемн. %, не более	0,1	0,1	0,2	0,1	0,1	0,2

1) Index
2) "Regent" mazouts
3) Light
4) Medium
5) Heavy
6) "Kift [sic] Oil Products" mazouts
7) Density at 15°C, tons/m³
8) Conventional viscosity, °VC at 50°C
9) Temperatures, °C
10) Flash point (closed crucible), °C, not below
11) Pour point, °C, not above
12) High heat of combustion, kcal/kg, not below
13) Ash, %, not above
14) Sulfur, %
15) Mechanical impurities, % by mass, not above
16) Water, % by volume, not above.

is recommended for nozzles with low throughput and evaporation-type nozzles.

Tables 4.13 and 4.14 give the specifications for mazouts used in Belgium and Japan.

TABLE 4.12

West German Specification DIN-51603 for Mazouts, 1960

1 Показатели	2 Мазут			
	3 сорт EL	Сорт L	Сорт M	Сорт S
4 Плотность при 15° C, $m/м^3$, не более	0,860	—	—	—
5 Температура вспышки (в закрытом тигле), °C, не ниже	55	55	65	56
6 Вязкость кинематическая, *сст*, не более:				
7 при 20° C	8	17	—	—
» 50° C	—	—	38	450
» 100° C	—	—	—	40
8 Вязкость условная, °ВУ, не более:				
7 при 20° C	~1,6	~2,5	—	—
» 50° C	—	—	5	~59
» 100° C	—	—	—	5,3
9 Температура застывания, °C, не более	—10	—5	0	—
10 Теплота сгорания (низшая) мазута, *ккал/кг*, не менее				
11 из нефти	10 000	9800	9600	9400
12 » каменного и бурого угля	—	9000	9000	9000
13 Подогрев				
14 перед транспортировкой	15 Не требуется	16 В отдельных случаях	16 В отдельных случаях	17 В основном требуется
18 перед сжиганием	19 То же	То же 19	В основном требуется 17	20 Требуется
21 Перегоняется до 95%, при температуре, °C, не выше	370	—	—	—
22 Коксуемость по Конрадсону, %, не более	0,05	2,0	10	15
23 Зольность, %, не более	0,01	0,04	0,07	0,15
24 Сера в мазуте, %, не более:				
11 из нефти	1.0	1,8	3,2	25 Не указывается
26 » каменного угля	—	1,0	1,0	1,0
27 » бурого угля	—	2,5	1,8	—
28 Механические примеси, %, не более	0,05	0,1	0,25	0,5
29 Вода, %, не более	0,1	0,3	0,5	0,5

1) Index
2) Mazout
3) Grade EL
4) Density at 15°C, tons/m³, not above
5) Flash point (in closed crucible), °C, not below
6) Kinematic viscosity, cSt, not above
7) At
8) Conventional viscosity, °VC, not above
9) Pour point, °C, not above
10) Heat of combustion (low) of mazout, kcal/kg, not below
11) From petroleum
12) From coal and lignite
13) Preheating
14) Before transport
15) Not required
16) In some cases
17) Usually required
18) Before burning
19) Same
20) Required

21) 95% distilled at temperature, °C, not above
22) Conradson coking capacity, %, not above
23) Ash, %, not above
24) Sulfur in mazout, %, not above
25) Not indicated
26) From coal
27) From lignite
28) Mechanical impurities, %, not above
29) Water, %, not above.

TABLE 4.13

Specification NBN 52096 cf Belgian Standardization Institute (1959)

1 Показатели	2 Газойль	3 Мазут			
		4 легкий	5 средний	6 тяжелый	7 сверхтяжелый
8 Вязкость кинетическая, *ccm*, не более:					
9 при 20° C	9,7	18,5	130	—	—
» 37,8° C	5,7	9,3	48,9	196	981
» 50° C	—	—	—	106	418
10 Вязкость условная, °ВУ, не более:					
9 при 20,0° C	1,8	2,1	17,0	—	—
» 37,8° C	1,46	1,8	6,5	25,6	129
» 50,0° C	—	—	—	14,0	55
11 Температура, °C:					
12 вспышки (в закрытом тигле), не менее	55	55	65	65	65
13 застывания, не выше	−6	0	—	—	—
14 Перегоняется до 370° C, %, не более	90	—	—	—	—
15 Сера, %, не более	1,2	2,0	2,7	3,8	4,8
16 Вода и механические примеси, %, не более	0,1	0,5	1,0	1,5	2,0

1) Index
2) Gas oil
3) Mazout
4) Light
5) Medium
6) Heavy
7) Superheavy
8) Kinematic viscosity, cSt, not above
9) At
10) Conventional viscosity, °VC, not above
11) Temperatures, °C
12) Flash point (closed crucible), not below
13) Pour point, not above
14) Distilled below 370°C, %, not above
15) Sulfur, %, not above
16) Water and mechanical impurities, %, not above.

TABLE 4.14

ISK Specification 2205-58 for Mazouts as Applied in Japan

1 Показатели	2 Мазут А		2 Мазут В	2 Мазут С			
	I	II		I	II	III	IV
3 Вязкость кинематическая при 50° С, *сст*, не выше	20	20	80	50—150	50—150	150—400	4 Выше 400
5 Вязкость условная, °ВУ, не выше	2,95	2,95	6,81	6,81—20,25	6,81—20,25	20,25—54,0	4 Выше 54
6 Температура, °С							
7 вспышки (в закрытом тигле), не ниже	60	60	60	70	70	70	70
8 застывания, не выше	5	6	10	—	—	—	—
9 Коксуемость в остатке, %, не более	4	4	8	—	—	—	—
10 Зольность, %, не более	0,05	0,05	0,05	0,1	0,1	0,1	—
11 Сера, %, не более . .	0,5	2,0	3,0	1,5	3,5	—	—
12 Вода и механические примеси, %, не более	0,3	0,3	0,4	0,5	0,5	0,6	2,0

1) Index
2) Mazout
3) Kinematic viscosity at 50°C, cSt, not above
4) Above
5) Conventional viscosity, °VC, not above
6) Temperatures, °C
7) Flash point (closed crucible), not below
8) Pour point, not above
9) Coking capacity in residue, %, not above
10) Ash, %, not above
11) Sulfur, %, not above
12) Water and mechanical impurities, %, not above.

4. BASIC PROPERTIES OF LIQUID BOILER FUELS

The quality requirements laid down for boiler fuels are determined by a number of physicochemical indices: heat of combustion, viscosity, flash and pour points, mechanical-impurity content, contents of ash, sulfur, water and gums. These indices make it possible to specify fields and conditions of application for the various fuel grades.

Heat of Combustion and Elementary Composition

The heat of combustion of a boiler fuel is an important index, one on which the rate of fuel consumption depends. For fuels used on seagoing vessels, a high heat of combustion is particularly important, since it makes it possible to increase the range of the vessel for a given loaded weight of fuel. Heat of combustion depends on fuel elementary composition. The high heats of combustion of liquid fuels are explained by their high hydrogen and carbon contents and low ash contents. The oxygen (O), nitrogen (N), moisture (W) and noncombustible mineral substances, the ash (A), that

enter into the composition of the fuel represent ballast.

High and low heats of combustion are distinguished. In determining the high heat of combustion, the amount of heat liberated on condensation of the water vapor formed on combustion of the hydrogen in the fuel and that present in the fuel itself is counted in addition to the heat liberated on combustion of the fuel.

The heat expended on the formation of water is not counted in determining the low heat of combustion.

The Mendeleyev formula is used most commonly in determining heats of combustion.

In thermal calculations, boiler fuels are characterized:

a) by the working mass of fuel, which indicates what fuel is going into the firebox:

$$C^p + H^p + O^p + N^p + S_л^p + A^p + W^p = 100\%$$

b) by the dry (water-free) mass of the fuel:

$$C^c + H^c + O^c + N^c + S_л^c + A^c = 100\%$$

c) by the combustible mass of fuel, which represents the water-free and ash-free composition of the fuel:

$$C^r + H^r + O^r + N^r + S_л^r = 100\%$$

In the formula, S_1 is volatile combustible sulfur.

Thermal calculations for boilers are usually made on the basis of working fuel mass. The conversion from one fuel mass to another is made with the aid of the multipliers given in Table 4.15.

For example, if we know C^g, then C^r is determined by the formula

$$C^p = C^r \frac{100 - W^p - A^p}{100}$$

The low heat of combustion of a fuel (in kcal/kg), Q_n^r, is computed by the formulas

$$Q_н^p = Q_в^p - 6(W^p + 9H^p)$$

$$Q_н^c = Q_в^c - 54H^c$$

$$Q_н^r = Q_в^r - 54H^r$$

$$Q_н^p = Q_н^r \frac{100 - W^p - A^p}{100} - 6W$$

Table 4.16 lists typical characteristics of fleet and firebox mazouts recommended for calculations by Norm S-1-1685-54 and the standardized methods.

TABLE 4.15

Auxiliary Factors for Fuel-Composition Conversion

A Заданная масса топлива	B Искомая масса топлива		
	C рабочая	D сухая	E горючая
C Рабочая	1	$\frac{100}{100-W^p}$	$\frac{100}{100-W^p-A^p}$
D Сухая	$\frac{100-W^p}{100}$	1	$\frac{100}{100-A^c}$
E Горючая	$\frac{100-W^p-A^p}{100}$	$\frac{100-A^c}{100}$	1

A) Given fuel mass
B) Sought fuel mass
C) Working
D) Dry
E) Combustible.

TABLE 4.16

Composition of Working Masses of Fleet and Firebox Mazouts as Recommended for Calculations

1 Мазут	2 Состав, %							3 Низшая теплота сгорания $Q^p_н$, ккал/кг	4 Теплота сгорания (в бомбе) $Q^p_б$, ккал/кг	5 Примечание
	C^p	H	S^p	O^p	N^p	A^p	W^p			
6 Флотский	84,42	11,47	0,8	0,7	0,21	0,15	2,0	9650		7 По нормали С-1-1685—54 [8]
8 Малосернистый топочный	85,3	10,2	0,5	0,7		0,3	3,0	9310	10 210	Нормативный 9 метод
10 Высокосернистый топочный	83,4	10,0	2,9	0,4		0,3	3,0	9170	10 060	[9]

1) Mazout
2) Composition, %
3) Low heat of combustion Q^r_n, kcal/kg
4) Heat of combustion (in bomb) Q^r_b, kcal/kg
5) Remarks
6) Fleet
7) According to Norm S-1-1685-54 [8]
8) Low-sulfur firebox
9) Standardized method
10) High-sulfur firebox.

TABLE 4.17

Average Elementary Compositions of Various Fuels

1 Топливо	2 Элементарный состав, %					
	C^p	H^p	$S^p_л$	O^p+N^p	W^p	A^p
3 Мазут Ф12 малосернистый	84,68	12,05	0,71	1,59	0,94	0,03
4 Мазут Ф12 сернистый . .	85,74	11,10	2,05	0,92	0,16	0,03
5 Мазут топочный сернистый:						
6 $ВУ_{50}=20$	84,87	11,18	2,11	1,81	0,00	0,03
7 марки 40	85,15	10,75	2,00	2,08	0,00	0,02
8 Ярегская нефть	85,29	11,58	1,16	0,95	0,99	0,03

1) Fuel
2) Elementary composition, %
3) Low-sulfur mazout F12
4) Sulfur-containing mazout F12
5) Sulfur-containing firebox mazout
6) VC_{50} = 20
7) Grade No. 40
8) Yarega petroleum.

TABLE 4.18

Elementary Compositions and Heats of Combustion of Low-Viscosity Mazouts (according to R.K. Platonov [5])

1 Мазут	2 Элементарный состав, %					Теплота сгорания, 3 $Q^c_н$, ккал/кГ
	C^c	H^c	S^c	A^c	N^c+O^c	
4 Ф12 малосернистый	86,92	12,09	0,33	0,07	0,59	9930
5 Ф20 малосернистый	87,10	11,70	0,50	0,10	0,60	9870
6 Ф5 сернистый	85,85	12,16	1,69	0,04	0,26	9920
7 Крекинг-мазут Ф12, сернистый	84,80	11,18	2,05	0,06	1,91	9860
8 Дистиллятный из сланцевой смолы	82,60	10,16	0,55	0,04	6,65	8810

1) Mazout
2) Elementary composition, %
3) Heat of combustion $Q^S_Л$, kcal/kg
4) Low-sulfur F12
5) Low-sulfur F20
6) Sulfur-containing F5
7) F12 cracking mazouts, containing sulfur
8) Distillate mazout from shale tar.

TABLE 4.19

Elementary Compositions of Firebox Mazouts [6]

1 Сорт	2 Элементарный состав, %			
	$C^г$	$H^г$	$S^г$	$O^г + N^г$
3 Мазут				
4 $ВУ_{50} = 20$	87,2	11,7	0,5	0,6
40	87,4	11,2	0,5	0,9
$ВУ_{80} = 60$	87,6	10,7	0,7	1,0
100	87,6	10,5	0,7—1	1,0
5 малосернистый	87,8	10,7	0,7	0,8
6 высокосернистый	84,0	11,5	3,5	0,5

1) Grade
2) Elementary composition, %
3) Mazout
4) $VC_{50} = 20$
5) Low-sulfur
6) High-sulfur.

TABLE 4.20

Elementary Composition and Heats of Combustion of High-Viscosity Cracking Residues [3]

1 Исходное сырье	2 Вязкость условная, °ВУ, при		3 Плотность ρ_4^{20}	4 Элементарный состав, %					5 Теплота сгорания		
	50° C	80° C		$C^г$	$H^г$	$S^г$	$O^г + N^г$	A^c	$Q_в^г$	$Q_н^г$	$K_в^г$ (объемная) 6
									7 ккал/кг		ккал/л 8
9 Туймазинский мазут	2728,0	119,1	1,0580	86,96	9,83	2,17	1,04	0,25	9 967	9436	10 544
	1041,0	73,0	1,0441	86,45	9,60	2,19	1,76	0,17	10 048	9530	10 491
	440,0	40,2	1,0315	87,15	10,19	1,70	0,96	0,23	10 065	9515	10 382
	189,8	22,3	1,0039	87,65	10,38	1,48	0,47	0,11	10 243	9683	10 283
10 Бакинский мазут	881,5	56,8	1,0062	89,14	9,66	0,59	0,61	0,09	10 131	9609	10 194
	531,0	43,5	1,0050	87,67	10,29	0,30	1,74	0,17	10 261	9708	10 312
9 Туймазинский мазут	424,0	37,2	1,0336	86,49	10,02	2,30	1,19	0,20	10 092	9551	10 431
11 Бугульминская нефть	124,4	16,5	1,000	86,35	10,25	2,38	1,02	0,17	10 175	9221	10 175

1) Original raw material
2) Conventional viscosity, °VC, at
3) Density
4) Elementary composition, %
5) Heat of combustion
6) (by volume)
7) kcal/kg
8) kcal/liter
9) Tuymazy mazout
10) Baku mazout
11) Bugul'ma petroleum.

The elementary compositions of boiler fuels have come to vary markedly as a result of more exhaustive refining processes and the use of sulfur-containing raw material.

The higher the viscosity and density of the mazout, the more carbon will it contain, because of the smaller hydrogen content. In viscous mazouts, the contents of sulfur, oxygen and nitrogen are higher. Viscous cracking mazouts contain from 87.0 to 88.5% carbon and from 10.5 to 11.5% hydrogen. Low-viscosity mazouts contain from 83.5 to 85.5% carbon and 11.4 to 12.2% hydrogen. The sulfur contents may reach 1% in viscous cracking mazouts from nonsulfuric petroleums and 3.5% in sulfur-containing mazouts.

The average elementary compositions and heats of combustion of mazouts and cracking residues are listed in Tables 4.17-4.20.

The heat of combustion of the combustible mass of a viscous cracking residue is 2.0-3.5% lower than those of straight-run mazouts. The difference between the heats of combustion of low-sulfur and normal-sulfur mazouts of the same grade ranges up to 2.0% (Table 4.21).

Under field conditions, an empirical relation linking heat of combustion with fuel density can be used for orientational calculations:

$$Q_{в} = 12\,400 - 2100\rho^{2}$$

or

$$Q_{н} = Q_{в} - 50.45$$

where ρ is the density at 15°C.

The hydrogen content in the fuel (in %) can also be determined on the basis of the 15°C density:

$$H = 26 - 15\rho$$

Figure 4.1 shows the high and low heats of combustion as functions of density [10].

The working heat of combustion of a fuel containing water (watered fuel) can be calculated by the formula

$$Q_{раб.обв.} = Q_{н} - 0.01\,Q_{н} \cdot W - 5.58\,W$$

where W is the water content in the fuel in %.

The heat of combustion can be computed approximately by the formula

$$Q_{раб.обв} = Q_{н} - 100W$$

Table 4.22 shows the decrease in the heat of combustion of a mazout as a function of the degree to which it is watered [5]. Figure 4.2 is convenient for quick orientational determination of the heat of combustion of a watered fuel. Operating personnel are essentially interested in the heat of combustion calculated per unit volume (volumetric heat of combustion):

TABLE 4.21

Heats of Combustion of Low-Sulfur and High-Sulfur Mazouts (Dried [1])

1 Топливо	2 Теплота сгорания, $Q_н^с$, ккал/кг	1 Топливо	2 Теплота сгорания, $Q_н^с$, ккал/кг
3 Малосернистый мазут условной вязкостью (°ВУ) при 50° С:		Высокосернистый мазут условной 4 вязкостью (°ВУ) при 50° С:	
10	10 000—9 950	10	9850—9750
20	9 870—9 650	20	9680—9460
40	9 750—9 420	40	9610—9280
60	9 700—9 350	60	9560—9350
80	9 760—9 240	80	9530—9280
100	9 640—9 100	5 100	9500—9100
		Каменноугольная сланцевая смола	9000—8200

1) Fuel
2) Heat of combustion $Q_{н}^{s}$, kcal/kg
3) Low-sulfur mazout with 50°C conventional viscosity (°VC) of
4) High-sulfur mazout with 50°C conventional viscosity (°VC) of
5) Coal-shale tar.

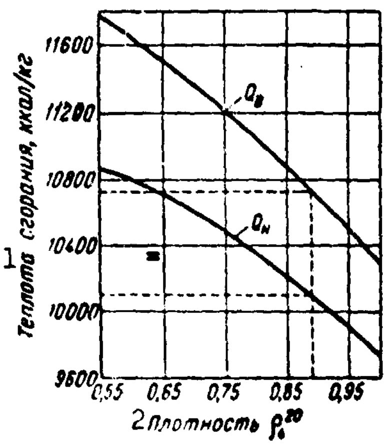

Fig. 4.1. High and low heats of combustion of fuels (dried) as functions of density. 1) Heat of combustion, kcal/kg; 2) density.

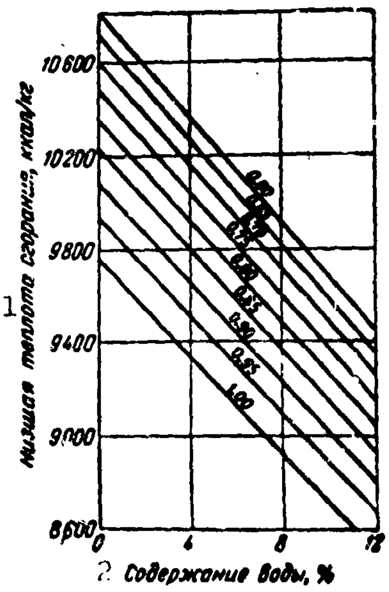

Fig. 4.2. Low-heat of combustion of fuel as a function of water content. The numerals on the lines are densities. 1) Low heat of combustion, kcal/kg; 2) water content, %.

TABLE 4.22

Decrease in Heat of Combustion of Mazout as a Function of Watering [5]

A Содержание воды, %	B Потери Q, ккал/кг: C от примеси воды	B Потери Q, ккал/кг: D от эвакуации образовавшейся воды в испаренном состоянии	E Сумма потерь, ккал/кг	F $Q_н^р$, ккал/кг	G Потери (считая от $Q_в^А$ = 10 465), %	A Содержание воды, %	B Потери Q, ккал/кг: C от примеси воды	B Потери Q, ккал/кг: D от эвакуации образовавшейся воды в испаренном состоянии	E Сумма потерь, ккал/кг	F $Q_н^р$, ккал/кг	G Потери (считая от $Q_в^А$ = 10 465), %
0	—	626	626	9839	6	10	1050	686	1736	8729	16,6
1	105	632	737	9728	7	15	1575	716	2291	8174	21,9
2	210	638	848	9617	8,1	20	2100	746	2846	7619	27,2
3	315	644	959	9606	9,1	25	2625	776	3401	7064	32,5
5	525	656	1181	9286	11,3	30	3150	800	3950	6515	37,7

A) Water content, %
B) Loss of Q, kcal/kg
C) Due to water impurity
D) From evacuation of formed water in vaporized state
E) Sum of losses, kcal/kg
F) kcal/kg
G) Losses (figured from Q_V^A = 10,465), %.

$$K_{н}^{р} = Q_{н}^{р} \rho_{4}^{20}$$

The volumetric heats of combustion of cracking mazouts are usually larger than those of straight-run mazouts.

For comparing fuels and solving substitution problems, as well as for establishing norms for consumption and requirement planning, a conventional unit heat of combustion equal to 7000 kcal/kg has been introduced. A fuel with a working-mass heat of combustion of 7000 kcal/kg is known as a conventional fuel.

Fuels are compared on the basis of fuel calorie equivalent, which is determined by the formula

$$Э_{кал.} = \frac{Q_{н}^{р}}{Q_{усл}} = \frac{Q_{н}^{р}}{7000}$$

The calorie equivalent for mazout is 1.4.

To evaluate mazouts as fuels, thermal-engineering characteristics calculated by the formulas given in Table 4.23 are employed. The thermal-engineering characteristics of mazouts and tars calculated by these formulas are given in Tables 4.24-4.26. Table 4.27 shows the theoretical volumes of air and mazout combustion products that are recommended for calculations.

TABLE 4.23

Formulas for Figuring Thermal-Engineering Characteristics of Fuel

1 Теплотехнические характеристики	2 Формулы
3 β — характеристика топлива	$\beta = 2{,}37\,\frac{H^{г} - 0{,}126\,O^{г}}{K^{г}} + 0{,}005$ 4 где $K^{г} = 0{,}3685\,S^{г}_{л} + C^{г}$ %
5 $L^{г}_{0}$ — теоретически необходимое количество воздуха на 1 кг горючей массы топлива, кг/кг	$L^{г}_{0} = 0{,}115\,C^{г} + 0{,}344\,H^{г} + 0{,}043\,(S^{г} - O^{г})$
6 RO_2 — максимальное содержание продуктов полного сгорания C и S в дымовых газах ($CO_2 + SO_2 = RO_2$), %	$RO_2^{макс.} = \frac{20{,}9}{1+\beta}$
7 Максимальное содержание SO_2 в сухих дымовых газах, %	$SO_2^{макс.} = V^{г}_{SO_2} \cdot \frac{100}{V^{г}_{сг}} = 0{,}367 \cdot \frac{K^{г}}{RO_2^{макс.}}$
8 $V^{г}_{SO_2}$ — объем SO_2 на 1 кг горючей массы топлива, нм³/кг	$V^{г}_{SO_2} = \frac{2S^{г}_{л}}{\varrho_{SO_2} \cdot 100} = 0{,}00683\,S^{г}_{л}$ 4 где $\varrho_{SO_2} = 2{,}927$ нм³/кг 9
10 $V^{г}_{сг}$ — объем сухих газов на 1 кг горючей массы топлива, нм³/кг	$V^{г}_{сг} = 1{,}86\,\frac{K^{г}}{RO_2^{макс.}}$
11 $V^{г}_{вп}$ — объем водяных паров в продуктах горения 1 кг горючей массы топлива, нм³/кг	$V^{г}_{вп} = \frac{9H^{г} + L^{г}_{0}}{80 \cdot 5}$
12 $V^{г}_{влг}$ — объем влажных газов на 1 кг горючей массы топлива, нм³/кг	$V^{г}_{влг} = V^{г}_{сг} + V^{г}_{вп}$
13 p_{SO_2} — парциальное давление SO_2, кГ/см²	$p_{SO_2} = 1{,}033\,\frac{V^{г}_{SO_2}}{V^{г}_{влг}}$
14 p_{H_2O} — парциальное давление водяного пара, кГ/см²	$p_{H_2O} = 1{,}033\,\frac{V_{H_2O}}{V^{г}_{влг}}$
15 $T^{г}_{гор.}$ — теоретическая температура горения, °C	$T^{г}_{гор.} = \frac{Q^{г}_{н}}{V^{г}_{сг} c_{сг} + V^{г}_{вп} c_{вп}}$

Note. c_{sg} and c_{vp} are the heat capacities per unit volume of the dry gases and water vapor in kcal/(m³(NTP)·deg).

1) Thermal-engineering characteristics
2) Formulas
3) β – fuel characteristic
4) Where
5) L^{g}_{0} – the theoretically necessary quantity of air for 1 kg of fuel combustible mass, kg/kg
6) RO_2 – the maximum content of products of complete combustion of C and S in the smoke gases ...
7) Maximum SO_2 content in dry smoke gases, %
8) $V^{g}_{SO_2}$ – volume of SO_2 to 1 kg of fuel combustible mass, m³(NTP)/kg

9) m^3(NTP)/kg

10) V^g_{sg} – volume of dry gases to 1 kg of fuel combustible mass, m^3(NTP)/kg

11) V^g_{vp} – volume of water vapor in combustion products of 1 kg of fuel combustible mass, m^3(NTP)/kg

12) V^g_{vlg} – volume of moist gases to 1 kg of fuel combustible mass, m^3(NTP)/kg

13) p_{SO_2} – partial pressure of SO_2, kg/cm²

14) p_{H_2O} – partial pressure of water vapor, kg/cm²

15) T^g_{gor} – theoretical combustion temperature, °C.

TABLE 4.24

Thermal-Engineering Characteristics of Sulfur-Containing and Low-Sulfur Mazouts [14]

1 Мазут	2 Элементарный состав в пересчете на горючую массу, %				3 Характеристика топлива β	4 Коэффициент $K^г$	5 Теоретически необходимое количество воздуха		8 Содержание в дымовых газах, %		9 Объем продуктов сгорания при теоретическом избытке воздуха, нм³/кг				10 Парциальное давление, кГ/см²		11 Теоретическая температура горения $T^г_{гор.}$, °C
	$C^г$	$H^г$	$S^г$	$O^г+N^г$			6 $L^г_0$, кг/кг	7 $V^г_0$, нм³/кг	RO_2 макс.	SO_2 макс.	$V^г_{SO_2}$	$V^г_{сг}$	$V^г_{вп}$	$V^г_{влг}$	p_{SO_2}	p_{H_2O}	
12 Высокосернистый вязкостью °ВУ при 50° С:																	
5,3	85,41	11,49	3,10	0,0	0,320	86,55	13,91	10,76	15,8	0,21	0,0212	10,19	1,46	11,65	0,00188	0,1295	2070
7,9	85,43	11,48	3,04	0,0	0,316	86,60	13,91	10,76	15,8	0,20	0,0203	10,19	1,46	11,65	0.00184	0,1295	2070
10,9	84,36	11,52	3,50	0,62	0,322	85,65	13,79	10,66	15,8	0,24	0,0239	10,08	1,46	11,54	0,00214	0,1307	2080
13 Малосернистый вязкостью (°ВУ) при 50° С:																	
4,94	86,54	12,52	0,42	0,52	0,348	86,69	14,25	11,02	15,5	0,03	0,0029	10,40	1,58	11,98	0,00025	0,1362	2060
17,9	87,70	11,43	0,54	0,33	0,312	87,90	14,08	10,85	15,9	0,04	0,0037	10,25	1,45	11,73	0,00033	0,1277	2080
58,6	87,53	10,69	0,72	1,06	0,291	87,80	13,73	10,62	16,2	0,05	0,0049	10,14	1,56	11,50	0,00044	0,1222	2090

1) Mazout
2) Elementary composition converted to combustible mass, %
3) Fuel characteristic β
4) Coefficient
5) Theoretically necessary amount of air
6) kg/kg
7) m^3(NTP)/kg
8) Content in smoke gases, %
9) Volume of combustion products at the retical air excess, m^3(NTP)/kg
10) Partial pressure, kg/cm²
11) Theoretical combustion temperature
12) High-sulfur mazout, 50°C viscosity in °VC of
13) Low-sulfur mazout, 50°C viscosity (°VC) of.

TABLE 4.25

Elementary Compositions and Thermal-Engineering Characteristics of Mazout-Substitute Tars [6]

1 Смола	2 Способ получения	3 Плотность при 20° С, г/см³	4 Вязкость условная при 50° С, °ВУ	5 Элементарный состав, % — 6 горючая масса: $C^г$	$H^г$	$S^г$	$N^г+O^г$	7 балласт: $W^р$	$A^р$	8 Теплота сгорания $Q^р_н$, ккал/кг	9 Коэффициент $K^г$, %	10 Характеристика топлива β	11 Теоретически необходимое количество воздуха $L^г_0$, кг/кг	12 Максимальное содержание в сухих газах $RO_2^{макс}$, %	13 Объем сухих газов $V^{мин}_{сг}$ при α=1, нм³/кг	14 Объем водяных паров в продуктах горения $V^{мин}_{вп}$ при α=1, нм³/кг	15 Теоретическая температура горения $T^г_{гор}$, °С
16 Каменноугольная	17 Коксование	1,04—1,2	24	90	7	1	2	18 Приблизительно 5	18 Приблизительно 1	8500	90,4	0,175	12,3	17,75	9,50	1,0	2040
19 Буроугольная	20 Газификация	1,1—1,2	55	83	7	2	8			8000	83,7	0,17	11,6	17,80	8,76	1,0	2060
	21 Полукоксование	0,98—1,1	10	85	11	1	3			8900	85,4	0,29	12,9	16,20	9,60	1,45	2000
22 Торфяная	20 Газификация	0,95—1,1	26	85	9	1	10			8000	80,4	0,225	11,6	17,10	8.73	1,20	2000
	21 Полукоксование	0,96	5	87	10,3	0,2	2			9000	87,1	0,27	13,0	16,50	9,80	1,38	2060
23 Сланцевая	24 Туннельный	0,96	1,6	84	10,5	0,5	5			8700	84,2	0,27	12,6	16,50	9,52	1,39	2000
	20 Газификация	1,00	4,7	83	10	1	6			8500	83,4	0,28	12,3	16,60	9,35	1,34	2000
25 Древесная	26 Сухая перегонка	1—1,2	20	72	8,75	—	19			7400	72	0,21	10,7	17,30	7,8	1,16	2060

1) Tar
2) Method of extraction
3) Density at 20°C, g/cm³
4) Conventional viscosity at 50°C, °VC
5) Elementary composition, %
6) Combustible mass
7) Ballast
8) Heat of combustion $Q^г_н$, kcal/kg
9) Coefficient ...
10) Fuel characteristic β
11) Theoretically necessary quantity of air L^g_0, kg/kg
12) Maximum content RO_2^{maks} in dry gases, %
13) Volume of dry gases V^{min}_{sg} at α = 1, m³(NTP)/kg
14) Volume of water vapor in combustion products, V^{min}_{vp} at α = 1, m³(NTP)/kg
15) Theoretical combustion temperature ...
16) Coal
17) Coking
18) Approximately
19) Lignite
20) Gasification
21) Semicoking
22) Peat
23) Shale
24) Tunnel
25) Wood
26) Dry distillation.

TABLE 4.26

Thermal-Engineering Characteristics of Commercial Firebox Mazouts [6]

1 Мазуты	2 Коэффициент $K^г$, %	3 Характеристика топлива β	4 Теоретически необходимое количество воздуха $L_0^г$, кг/кг	5 Максимальное содержание продуктов сгорания в сухих газах $RO_2^{макс}$, %	6 Объем сухих газов $V_{сг}^{мин}$ при α=1, нм³/кг	7 Объем водяных паров в продуктах горения $V_{вп}^{мин}$ при α=1, нм³/кг	8 Теоретическая температура горения $T^г_{гор}$, при α=1, °С
9 Мазут:							
10 20, ГОСТ 1501—57	87,38	0,321	14,06	15,82	10,27	1,48	2080
40	87,58	0,305	13,90	16,00	10,18	1,42	2080
60, ГОСТ 1501—57	87,86	0,291	13,75	16,19	10,09	1,37	2090
100	87,90	0,290	13,70	16,20	10,08	1,35	2090
11 малосернистый . . .	88,06	0,285	13,80	16,30	10,00	1,40	2090
12 высокосернистый	85,48	0,320	13,80	15,80	10,00	1,48	2050

1) Mazout
2) Coefficient ...
3) Fuel characteristic β
4) Theoretically necessary amount of air L_0^g, kg/kg
5) Maximum content of combustion products in dry gases, RO_2^{maks}, %
6) Volume of dry gases V_{sg}^{min} at α = 1, m³(NTP)/kg
7) Volume of water vapor in combustion products, V_{vp}^{min} at α = 1, m³(NTP)/kg
8) Theoretical combustion temperature T^g_{gor} at α = 1, °C
9) Mazout
10) 20, AUSS 1501-57
11) Low-sulfur
12) High-sulfur.

TABLE 4.27

Theoretical Volumes of Air and Mazout Combustion Products [9]

1 Мазут	2 Объемы, нм³/кг *				
	V^0	V_{RO_2}	$V^0_{N_2}$	$V^0_{H_2O}$	$V^0_г$
3 Малосернистый	10,28	1,60	8,12	1,34	11,06
4 Высокосернистый	10,15	1,58	8,02	1,32	10,92

*Volumes: V^0 – air; V_{RO_2} – triatomic gasee; $V^0_{N_2}$ – nitrogen; V_{H_2O} – water vapor; V^0_g – gases.

1) Mazout
2) Volumes, m³(NTP)/kg*
3) Low-sulfur
4) High-sulfur.

Heat Capacity and Thermal Conductivity

In solving problems of fuel preheating, and especially in determining the heating area of the coils and the amount of heat expended on preheating, it is necessary to know the heat capacity and thermal conductivity of the fuels.

The formulas given in Table 4.28 are recommended for determination of residual-fuel heat capacities [11, 12, 13].

Table 4.28 indicates the deviations of the calculated values from experimental data for determination of the heat capacities of mazouts and cracking residues. These heat capacities are listed in Table 4.3.

Better agreement between calculation and experiment is obtained with the Kragoye formula (error below 2.5%). According to literature data [12], the error ranges up to 5.9% at temperatures to 260°C when the Kragoye formula is used.

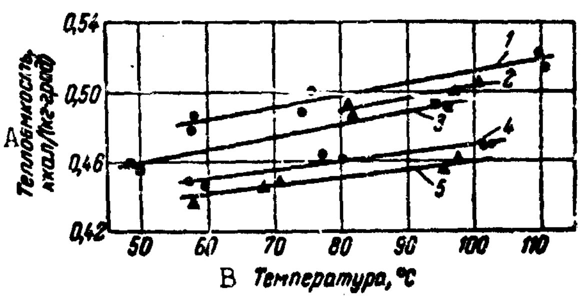

Fig. 4.3. Heat capacities of mazouts and cracking residues as functions of temperature: 1) mazout, $\rho_4^{20} = 0.904$; 2) mazout, $\rho_4^{20} = 0.914$; 3) mazout, $\rho_4^{20} = 0.931$; 4) cracking residue, $\rho_4^{20} = 1.009$; 5) cracking residue, $\rho_4^{20} = 1.044$. A) Heat capacity, kcal/(kg·deg); B) temperature, °C.

TABLE 4.28

Formulas for Heat Capacity

A Формулы	Для нефтепродуктов плотностью B ρ_{15}^{15}	Температурные пределы, C °C	Расхождения между расчетными и экспериментальными данными, D % (±)
1. Фортча и Уатмена: $c = (0{,}345 + 0{,}000886\,t) \times (2{,}1 - \rho_{15}^{15})$	0,75—1,00	E До 260	E До 4
2. К. С. Крэгое: $c = \frac{1}{\sqrt{\rho_{15}^{15}}}(0{,}403 + 0{,}00081\,t)$	0,72—0,96	0—400	До 2,5
3 ВТИ: $c = 0{,}415 + 0{,}0006\,t$	F Для топочных мазутов от 20 до 100° C; для крекинг остатков от 80 до 120° C		G Для крекинг-остатков $\rho_4^{20} = 0{,}9 - 3$; Для мазутов $\rho_4^{20} = 0{,}9 - 7{,}5$

A) Formula
B) For petroleum products with density ρ_{4}^{15} of
C) Temperature range, °C
D) Disagreement between calculated and empirical data, % [3]
E) To
F) 20 to 100°C for firebox mazouts; from 60 to 120°C for cracking residues
G) For cracking residues
H) For mazouts
1. Fortsch and Whitman
2. K.S. Kragoye
3. VTI.

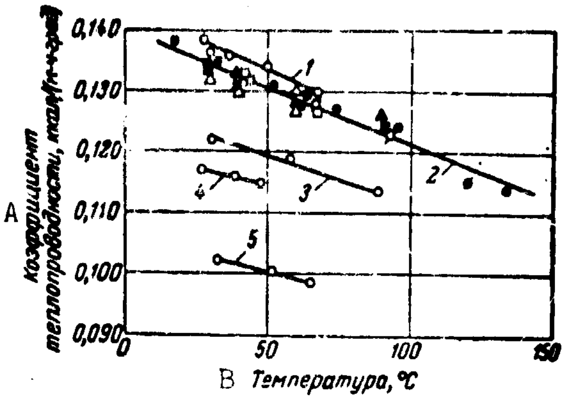

Fig. 4.4. Thermal-conductivity coefficient as a function of temperature: 1) Baku semiasphalt from asphalt, $\rho_{15} = 0.959$ g/cm^3, $VC_{100} = 16$ (experiments of N.B. Vargaftik); 2) high-viscosity cracking residues; 3) straight-run Krasnovodsk mazout, $\rho_{20} = 0.905$ g/cm^3, $VC_{80} = 3.9$ (experiments of Z.I. Geller); 4) cracking mazout from Groznyy refinery, $\rho_{15} = 0.973$ g/cm^3, $VC_{50} = 31.4$ (experiments of N.B. Vargaftik); 5) mazout, $\rho_{15} = 0.906$ g/cm^3, $VC_{50} = 4.94$ (experiments of N.B. Vargaftik). A) Coefficient of thermal conductivity, kcal/(m·h·deg); B) temperature, °C.

TABLE 4.29

Thermal Conductivity Coefficients of Mazouts

1 Мазут	2 Коэффициент теплопроводности ккал/(м·ч·град) при температуре				
	30° C	40° C	50° C	60° C	70° C
3 Прямогонный $ВУ_{50} = 4{,}94$	0,103	0,102	0,101	0,099	0,098
4 Крекинг-мазуты $ВУ_{50} = 31{,}39$ и $ВУ_{50} = 60{,}8$	0,116	0,115	0,114	0,113	0,112

1) Mazout
2) Thermal conductivity coefficient in kcal/(m·h·deg) at temperature of
3) Straight-run, $VC_{50} = 4.94$
4) Cracking mazouts, $VC_{50} = 31.39$ and $VC_{50} = 60.8$.

For practical calculations, a heat capacity of 0.45 to 0.49 kcal/(kg·deg) is taken in the range from 0 to 100°C for mazouts, and 0.5-0.58 kcal/(kg·deg) for tars [6].

Table 4.29 gives thermal conductivities of mazouts [11, 14] (coefficient of thermal conductivity λ) in the range from 30 to 70°C. It is recommended that the thermal conductivity coefficient given in the table for a mazout with VC_{50} = 4.94 be taken for No. 20 mazouts, and that for mazouts with VC_{50} = 31.39 and 60.8 for Nos. 40 and 100, respectively [9]. For approximate calculations of tar thermal conductivities, it is recommended [6] that λ be taken equal to 0.1 kcal/(m·h·deg) for light tars and up to 0.15 kcal//(m·h·deg) for heavy tars. The thermal conductivities of high-viscosity [3] cracking residues are given in Fig. 4.4.

The thermal conductivity coefficient can be determined from an empirical formula with accuracy sufficient for practical purposes:

$$\lambda = \frac{101}{\rho}(1 - 0{,}00054\, t)$$

where ρ is the density of the petroleum products at 15°C, g/cm^3;
t is the temperature in °C at which the heat capacity is determined.

The error of the determination is ±10% for temperatures from 0 to 200°C.

Viscosities of Liquid Boiler Fuels

Viscosity is an important property of mazouts, one that determines the possibility and conditions of their application; drainage from railroad tank cars, tankers and barges; transport via pipelines; atomization by nozzles.

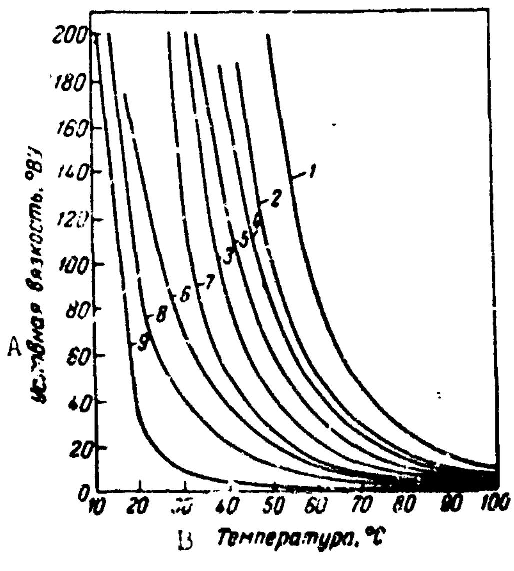

Fig. 4.5. Viscosities of mazouts as functions of temperature: 1, 2, 3) firebox mazouts, Nos. 200, 100, and 40, respectively; 4, 5, 6) firebox mazouts with VC_{50} = 80, VC_{50} = 60, and VC_{50} = 20, re-

spectively; 7) shale mazouts; 8, 9) fleet mazouts F12 and F5, respectively. A) Conventional viscosity, °VC; B) temperature, °C.

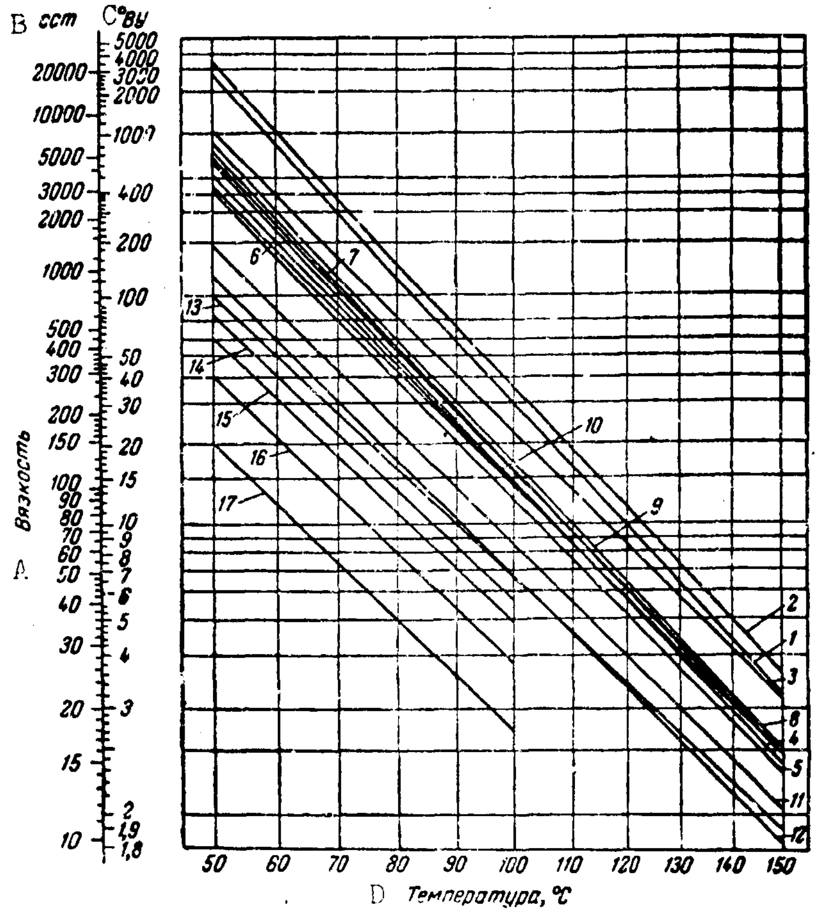

Fig. 4.6. Viscosity of cracking residues and mazouts as a function of temperature: 1, 3, 4, 5, 6, 11) Tuymazy mazouts with 20°C densities of, respectively, 1.058, 1.044, 1.044, 1.036, 1.034, 1.031, 1.004; 2, 7, 8, 9, 10) Baku mazouts with 20°C densities of, respectively, 1.046, 1.026, 1.022, 1.006, 1.005; 12) Bugul'ma petroleum with density of 1.0 at 20°C; 13, 14, 15, 16, 17) firebox mazouts, Nos. 100, 80, 60, 40, and 20, respectively. A) Viscosity; B) cSt; C) °VC; D) temperature, °C.

The conventional viscosities of mazouts have been adopted as the basic index for grading them. It is measured with a special viscosimeter and the viscosity value is expressed in conventional degrees (VC), which correspond to Engler degrees (E°).

The viscosities of mazouts at the temperatures indicated in the AUSS's cannot be used in drawing inferences as to their viscosity-temperature characteristics, since viscosity depends on temperature (Fig. 4.5). At high temperatures (70-100°C), a change in temperature has little influence on viscosity, while at temperatures from 50°C down, even minor temperature fluctuations may affect it strongly.

The dependence of the viscosities of mazouts on temperature is expressed in an alignment chart with the coordinate grid proposed by the ASTM. The straight lines, which characterize the change in viscosity with temperature for various grades of firebox mazouts in this coordinate grid, have almost identical slopes at above-zero temperatures, and may in first approximation be regarded as parallel [15].

Figure 4.6 shows the viscosities of cracking residues and firebox mazouts as functions of temperature, and Fig. 4.7 the viscosity-temperature relation for tars.

The heavier and more tarry the mazout, the higher the absolute value of its viscosity. However, in the low-temperature region (down from +50°C), the viscosities of mazouts depend on many factors: raw-material quality, method of extraction, paraffin and gum content.

Mazouts having practically identical viscosities at temperatures of 50°C and up and obtained from different petroleums or by different methods show different changes in viscosity as the temperature drops (Fig. 4.8). Straight-run paraffin-free mazouts from nonsulfurous raw material have a comparatively shallow viscosity-temperature curve down to 0°C, and even at temperatures below 0°C, their viscosities do not rise very sharply. Having low pour points at the same time, they can be transported and pumped relatively easily at temperatures around 0°C. The viscosities of paraffin-free cracking mazouts increase more rapidly with declining temperature than those of straight-run mazouts. However, even cracking mazouts usually retain mobility at temperatures near the pour point. As the viscosity increases with falling temperature, the limiting shear stress of paraffin-base mazouts rises sharply [51] as a result of crystallization of the high-melting, chiefly paraffinic hydrocarbons that they contain. Drainage and pump transfer of paraffin-base mazouts are possible only after they have been warmed to a temperature above the pour point.

Mazouts from sulfurous petroleums contain substantial quantities of paraffins and asphalt-tar substances (Table 4.30), and thus as the temperature falls, they not only show increased viscosity, but also lose mobility (fluidity) at temperatures higher than the pour points determined by the standard method.

From 10°C on down, the viscosities of sulfurous mazouts are many times those of mazouts that do not contain sulfur. At these temperatures, the nature of viscosity is also important for sulfur-containing mazouts. Table 4.30 shows two mazout viscosity values – the structural and residual viscosities, which correspond to undisturbed (maximum) and disturbed (minimum) structures.

In straight-run sulfur-containing and in cracking mazouts (Fig. 4.9), the ratio of maximum to minimum viscosity reaches 5-7 even at 0°C, and it is even larger at -10°C, while the same ratio does not exceed 1.4-1.6 for low-sulfur mazout. The viscosity increase associated with formation of structure greatly impedes pumping at low temperature. At temperatures down from 20°C, sulfur-containing cracking mazout pumps considerably more poorly than

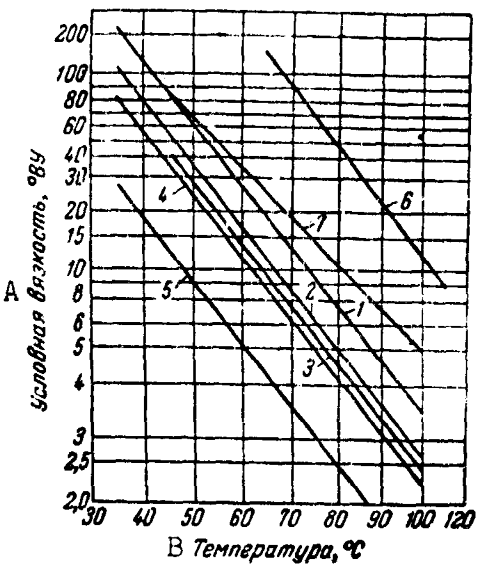

Fig. 4.7. Viscosity of tars as a function of temperature: 1) gas-generator tar from Chelyabinsk lignites; 2, 3, 4, 5) peat generator tars; 6) coal tar; 7) mazout, VC_{50} = 60. A) Conventional viscosity, °VC; B) temperature, °C.

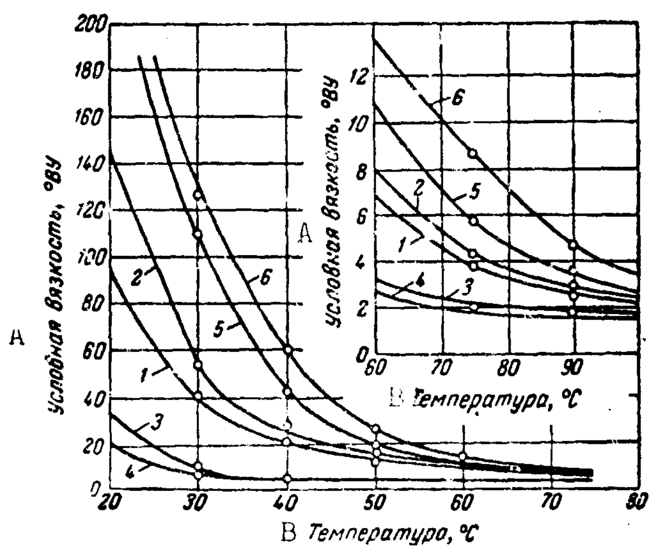

Fig. 4.8. Viscosity-temperature curves of straight-run and cracking mazouts: 1) straight-run F12 fleet mazout; 2) F12 sulfur-containing cracking mazout; 3, 4) straight-run F5 fleet mazout; 5) sulfur-containing cracking mazout with VC_{55} = 20; 6) straight-run No. 40 sulfur-containing mazout. A) Conventional viscosity, °VC; B) temperature, °C.

TABLE 4.30

Viscosity-Temperature Characteristics of Mazouts

1 Мазуты	2 Парафины, определенные: 3 методом Залозецкого-Голанда, %	2 Парафины, определенные: 4 адсорбцией на угле, %	5 Смолы, %	6 Асфальтены, %	7 Условная вязкость (°ВУ) при температуре: 50° C, 8 макс.	20° C, 9 мин.	10° C, 8 макс.	10° C, 9 мин.	0° C, 8 макс.	0° C, 9 мин.	−10° C, 8 макс.	−10° C, 9 мин.
10 Малосернистый Ф12 прямой перегонки	1,02	5,08	11,06	0,14	11,4	95,3	366	267	1 000	728	4 564	2 920
11 Сернистый крекинг-мазут Ф12	2,54	13,10	9,47	4,28	12	147,2	3668	903	17 736	3274	52 382	10 136
12 Сернистый Ф5 прямой перегонки . .	1,0	7,0	9,8	0,94	4,48	33,4	468	169	3 528	551	21 122	2 567

1) Mazouts
2) Paraffins, determined by
3) Zalozetskiy-Goland method, %
4) Adsorption on charcoal, %
5) Tars, %
6) Asphaltenes, %
7) Conventional viscosity (°VC) at temperature of
8) Maximum
9) Minimum
10) Straight-run low-sulfur F12
11) Sulfur-containing F12 cracking mazout
12) Straight-run F5 sulfur-containing mazout.

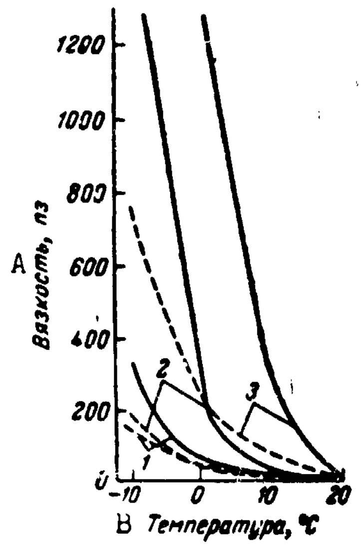

Fig. 4.9. Viscosity curves of low-sulfur and sulfur-containing mazouts at low temperatures: 1) straight-run F12 fleet mazout, VC_{50} = 12 (from low-sulfur petroleums); 2) straight-run fleet mazout, VC_{50} = 4.38 (from sulfur-containing petroleum), η_{maks} = 1465 (at -10°C); 3) cracking mazout, VC_{50} = 12 (from sulfur-containing petroleum), η_{maks} = 3813 (at -10°C); —— viscosity with undisturbed structure; --- viscosity with disturbed structure. A) Viscosity, poises; B) temperature, °C.

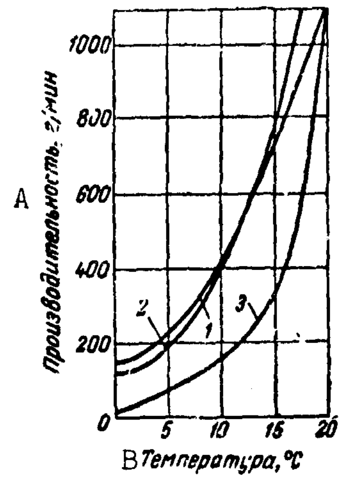

Fig. 4.10. Pumpability of mazouts as a function of temperature on laboratory apparatus: 1) straight-run F12 mazout, VC_{50} = 11.4; 2) straight-run sulfur-containing F5 mazout, VC_{50} = 4.48; 3) sulfur-containing F12 cracking mazout, VC_{50} = 12. A) Output, g/min; B) temperature, °C.

TABLE 4.31

Cooling of Petroleum Products as a Function of Time en route and Loading Temperature [16]

A Температура нефтепродуктов при наливе, °С	B Температура продуктов (в °С) при пробеге железнодорожных цистерн, сутки			
	8		5	
	C и при температуре воздуха во время перевозки			
	−10° C	−20° C	−10° C	−20° C
40	7	8	11	13
50	8	10	13	15
60	10	11	15	18
70	11	13	18	20
80	13	14	20	22

A) Temperature of petroleum products at loading, °C
B) Temperature of products (in °C) after ... days in railroad tank cars
C) And air temperature during shipment.

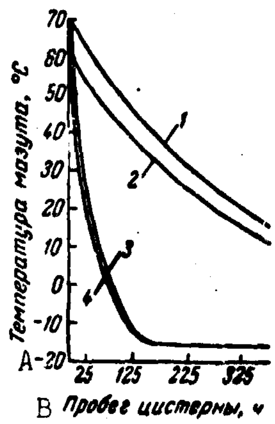

Fig. 4.11. Decrease in temperature of Nos. 40 and 80 mazouts during shipment in ordinary and thermos tank cars [52]; thermos cars: 1) No. 80 mazout; 2) No. 40 mazout; ordinary tank cars: 3) No. 80 mazout; 4) No. 40 mazout. A) Mazout temperature, °C; B) time in moving cars, hours.

TABLE 4.32

Viscosities of Various Mazout Grades at Low Temperatures

A Мазут	B Вязкость (в пз) при температурах				
	75° C	50° C	0° C	—10° C	—20° C
C Малосернистый флотский Ф12 . . .	0,351	1,077	72,4	320	54 723
D Сернистый 40	0,448	1,732	326	2320	2 260 000
E Сланцевый	0,377	1,676	404	3730	4 415 000

A) Mazout
B) Viscosity (in poises) at temperature of
C) F12 low-sulfur fleet
D) No. 40 sulfur-containing
E) Shale.

a low-sulfur mazout having the same viscosity as the cracking mazout at 50°C (Fig. 4.10).

During the winter, mazout in railroad tank cars, above-ground mazout pipelines without heat insulation, and above-ground storage tanks may acquire a rather low temperature. Table 4.31 presents data on the temperature decrease of petroleum products during shipment in railroad tank cars, and Fig. 4.11 presents curves of the temperature fall for Nos. 40 and 80 mazouts (AUSS 1501-57) during winter shipment [52] in four-axle railroad tank cars unloaded at temperatures of 60 and 70°C. At low temperatures, mazouts show quite high viscosities (Table 4.32), and they can be drained from tank cars only after warming to the following temperatures (in °C):

Fleet mazout:	
F12.	20
20.	30
Firebox mazout:	
20.	30
40.	40

60-80............................ 50-60
Mazout from paraffin-base petroleums. 40 and higher [11]

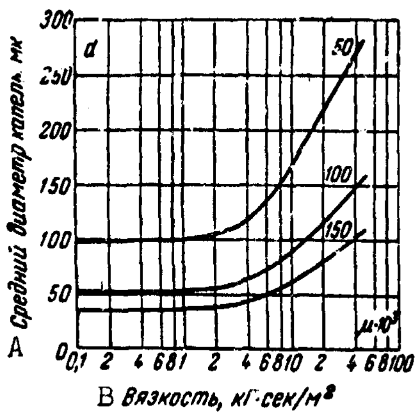

Fig. 4.12. Theoretical dependence of average drop diameter on viscosity. A) Average drop diameter, μm; B) viscosity, kg•s/m².

TABLE 4.33

Permissible Mazout Viscosities for Transfer by Pumps of Various Types and Required Pre-Heating Temperatures

A Тип насоса	B Предельная вязкость [15] °ВУ/сст	C Требуемые температуры (в °С) подогрева мазутов марок:							
		20	40	60	80	100	200	Ф12	Ф5
D Винтовые и шестеренчатые	E 200/1500 (ниже 10° ВУ снижают производительность)	20	28	35	38	42	50	15	12
F Центробежные производительностью 30—40 т/ч	30/~225	45	55	62	65	68	78	35	22
G Скальчатые и поршневые	H 75/550 (могут перекачивать мазуты вязкостью до 150° ВУ)	30	42	48	52	55	62	25	18

A) Pump type
B) Maximum viscosity [15], °VC/cSt
C) Required heating temperature (°C) for mazouts of grades No.
D) Screw and gear
E) 200/1500 (output drops at viscosities below 10°VC)
F) Centrifugal pumps rated at 30-40 tons/h
G) Plunger and piston types
H) 75/550 (mazouts with viscosities up to 150°VC can be transferred).

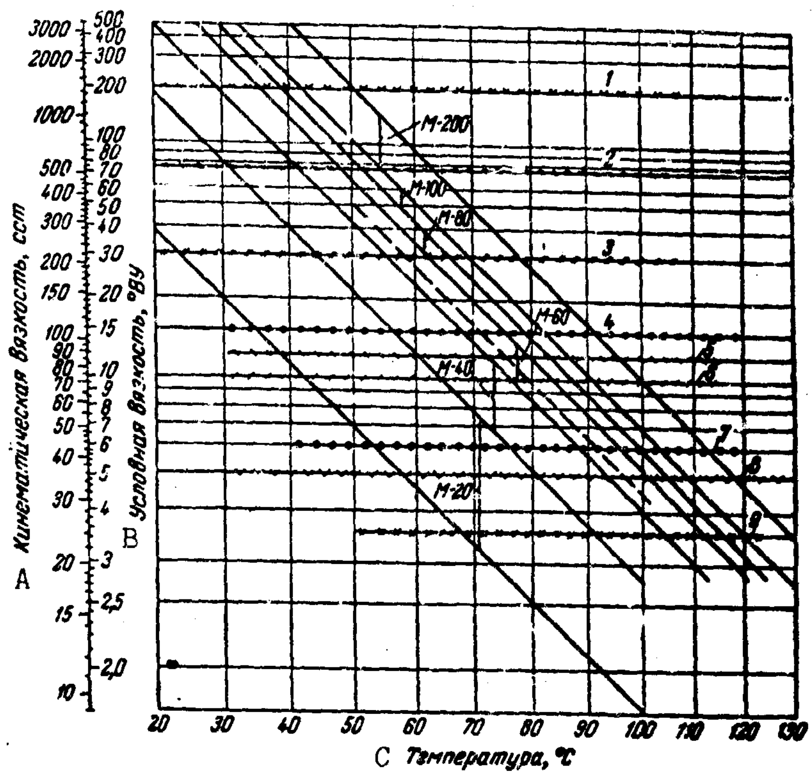

Fig. 4.13. VTI alignment chart for determination of mazout viscosity and temperature necessary for normal performance of various nozzles and pumps. Maximum mazout viscosities: 1) for screw and gear pumps; 2) for piston and plunger pumps; 3) for centrifugal pumps rated at 20-40 tons/h; 4) for steam nozzles; 5) for fan-type air nozzles; 6) for compressor air nozzles; 7) maximum mazout viscosity for mechanical nozzles and recommended viscosity for steam nozzles; recommended mazout viscosity; 8) for fan and compressor air nozzles; 9) for mechanical nozzles. A) Kinematic viscosity, cSt; B) conventional viscosity, °VC; C) temperature, °C.

It is also necessary to warm mazout to pump it through pipelines, since pump output declines with increasing viscosity of the mazouts; the efficiencies of centrifugal pumps fall at the same time.

The decrease in centrifugal-pump economy with increasing fuel viscosity can be appreciated from the Baklanov formula [15]:

$$\frac{\eta_{zh}}{\eta_v} = \frac{1}{(0.94 + \nu_{zh})^m}$$

where η_{zh} is the efficiency of the centrifugal pump for pumping a viscous liquid, %;

η_v is the pump efficiency in pumping water, %;

ν_{zh} is the kinematic viscosity, cm^2/s;

m is an exponent; $m = 0.6$ for a pump with an inlet pipe 100 mm in diameter.

Gear and screw pumps have stable efficiencies and small dimensions and set up an even nonpulsating pressure; they can be used to transfer mazouts with relatively high viscosities. Table 4.33 presents maximum mazout viscosities recommended by the VTI for transfer with various types of pumps. It also gives the required warming temperatures (taken from the alignment chart) for the various mazout grades.

Table 4.34 presents the recommended transfer rates for petroleum products with various viscosities.

Figure 4.12 [17] shows the theoretical dependence of average drop diameter on mazout viscosity for various transfer speeds on the assumption that the coefficient of surface tension, density, and geometrical dimension are constants.

The maximum viscosities of mazouts and their preheating temperatures can be determined from an alignment chart (Fig. 4.13) or Table 4.35 as functions of nozzle type.

For the mechanical nozzles of seagoing-vessel boiler installations, the mazout viscosity must be lower than for stationary boiler installations, and may not exceed 2-3°VC; to ensure such viscosity, fleet mazouts are heated to the following temperatures: F5 to 65-75°C, and F12 and F20 to 90 and 100°C, respectively.

TABLE 4.34

Recommended Transfer Speeds for Petroleum Products [16]

A Вязкость нефтепродуктов		B Средняя скорость перекачки, м/сек	
C кинематическая, сст	D условная °ВУ	E на линии всасывания	F на линии нагнетания
1—12	1—2	1,5	2,5
12—28	2—4	1,3	2,0
28—72	4—10	1,2	1,5
72—146	10—20	1,1	1,2
146—438	20—60	1,0	1,1
438—977	60—120	0,8	1,0

A) Viscosity of petroleum product
B) Average transfer speed, m/s
C) Kinematic, cSt
D) Conventional, °VC
E) On suction line
F) On delivery line.

TABLE 4.35

Required Viscosity and Preheating Temperature for Burning Mazouts with Various Types of Nozzles [15]

A Типы форсунок	B Вязкость мазута, °ВУ/сст		E Марка мазута	F Температура подогрева, °C	
	C допустимая	D рекомендуемая		G не ниже	D рекомендуемая
H Механические	6/~45	3,5/~25	20	75	90
			40	85	105
			60	95	110
			80	98	115
			100	103	120
			200	112	135
I Паровые	15/~120	6/~45	20	55	75
			40	65	85
			60	75	95
			80	77	90
			100	80	103
			200	90	112
J Воздушные высоконапорные (компрессорные)	10/~75	5/~35	20	65	80
			40	75	93
			60	80	100
			80	85	103
			100	90	108
			200	100	118
K Воздушные низконапорные (вентиляторные)	12/~90	5/~35	20	60	80
			40	72	93
			60	78	100
			80	82	103
			100	85	108
			200	95	118

A) Nozzle type
B) Mazout viscosity, °VC/cSt
C) Allowed
D) Recommended
E) Mazout grade
F) Preheating temperature, °C
G) Not below
H) Mechanical
I) Steam
J) High-pressure air (compressor)
Low-pressure air (fan).

TABLE 4.36

Influence of Heat Treatment on Viscosity Properties of Cracking Mazout with VC_{80} = = 11.84

1 Образцы	2 Условная вязкость (в °ВУ) при температуре			
	20° C	10° C	0° C	−10° C
3 До термообработки . . .	147,0	14 382	26 132	131 000
4 Непосредственно после термообработки . . .	125,0	552	2 710	12 240
5 Через 1 сутки после термообработки . . .	—	13 624	21 9[illegible]	121 000
6 Через 22 суток после термообработки . . .	—	14 100	24 300	133 280

1) Specimen
2) Conventional viscosity (°VC) at temperature of
3) Before heat treatment
4) Immediately after heat treatment
5) 1 day after heat treatment
6) 2 days after heat treatment.

TABLE 4.

Viscosities of Dry and Watered Mazouts at Various Temperatures

Мазуты	Содержание воды, %	Вязкость (в °ВУ) при температуре			
		75° C	50° C	30° C	20° C
Сернистый крекинг-мазут Ф-12:					
образец 1	Безводный	[illegible]	[illegible]	46,4	147,2
	5	[illegible]	[illegible]	—	318
образец 2	Безводный	3,98	11,2	53 0	161,4
	5	4,11	11,7	—	273,4
Сернистый крекинг-мазут топочный	Безводный	5,68	[illegible]	108,5	572
	5	6,14	24,0	115,5	691,4
Сернистый топочный прямой перегонки	Безводный	8,76	25,3	125,9	494
	5	9,64	32,4	—	594,7
Малосернистый топочный прямой перегонки	Безводный	5,91	23,6	136,4	—
	5	5,96	24,6	161,8	—

1) Mazout
2) Water content, %
3) Viscosity (°VC) at temperature of
4) F-12 sulfur-containing cracking mazout
5) Specimen
6) Dry
7) Sulfur-containing firebox cracking mazout
8) Sulfur-containing straight-run firebox mazout
9) Low-sulfur straight-run firebox mazout.

The viscosities of cracking mazouts and straight-run paraffin-base mazouts are not constant and depend on prior heat treatment and the degree of structural breakdown. Viscosity changes most sharply on preheating to 70-100°C; raising the heat-treatment temperature above 100°C has no marked influence on the viscosity variation. Preliminary heat treatment lowers the temperature at which the mazout shows distinct structure by almost 20°C [2, 11, 18]. The influence of 30 min of heat treatment at 100°C on the viscosity of sulfur-containing cracking mazout appears in Table 4.36.

The viscosities of mazouts also vary with degree of watering. Watering mazouts to 2-3% has practically no influence on viscosity. Mazouts containing up to 5% water show a particularly distinct viscosity increase at temperatures of 30°C and lower (Table 4.37). The viscosities of cracking mazouts increase to a greater degree on watering than do those of straight-run mazouts.

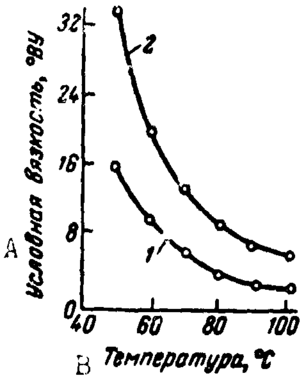

Fig. 4.14. Viscosity characteristics of watered fuel: 1) dry boiler fuel; 2) boiler fuel containing 15% water. A) Conventional viscosity, °VC; B) temperature, °C.

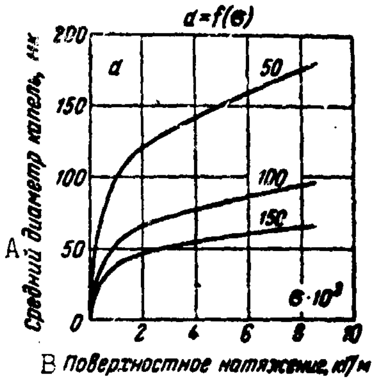

Fig. 4.15. Average drop diameter as function of surface tension. The n. ıer-als on the lines indicate relative velocity, m/s. A) Average drop diameter, μm; B) surface tension, kg/m.

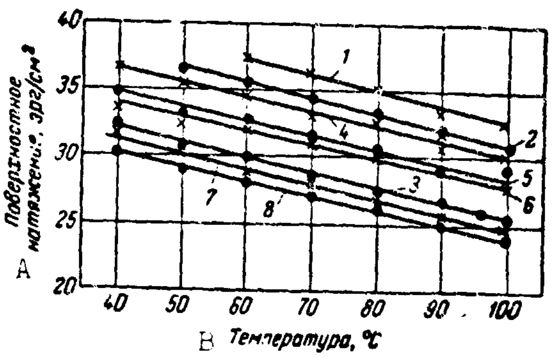

Fig. 4.16. Surface tension of mazouts as a function of temperature: sulfur-containing firebox cracking mazout: 1) VC_{50} = 60; 2) VC_{50} = 20; 3) VC_{50} = 14.1; sulfur-containing fleet cracking mazout: 4) VC_{50} = 12; 5) VC_{50} = 11.4; sulfur-containing straight-run fleet mazout: 6) VC_{50} = 4.38; 7) VC_{50} = 4.38; 8) low-sulfur fleet mazout with VC_{50} = 12. A) Surface tension, ergs/cm²; B) temperature, °C.

Figure 4.14 shows viscosity-temperature curves for dry cracking mazout and the same fuel containing up to 15% water [19]. With falling temperature, the difference between the viscosities of dry and watered mazouts will be even greater.

Surface Tension

The efficiency of fuel atomization depends on surface tension

as well as on viscosity. The higher the surface tension, the larger the fuel-droplet size when it is sprayed from nozzles (Fig. 4.15), the more difficult will it be to obtain fine atomization and good fuel-air mixing, and the poorer the combustion of the fuel.

TABLE 4.38

Surface Tension of High-Viscosity Cracking Mazouts [3]

1) Исходное сырье	2) Плотность ρ_4^{20}	3) Условная вязкость °ВУ при 80° C	4) Поверхностное натяжение дин/см при температуре 40° C	50° C	70° C	90° C	120° C
5) Туймазинский мазут	1,058	119,1	—	38,4	—	—	29,01
	1,044	73,0		36,1	31,5	30,3	28,1
	1,031	40,2	[illegible]	35,2	30,8	29,0	27,9
	1,004	22,3	38,7	35,0	—	29,8	27,9
6) Бакинский мазут	1,006	56,5	—	35,5	31,5	30,3	—
	1,005	43,5	40,0	35,8	30,2	30,0	27,9
7) Бугульминская нефть	1,000	16,5	37,5		29,0	28,4	26,5

1) Original raw material
2) Density
3) Conventional viscosity, °VC at 80°C
4) Surface tension, dynes/cm, at temperature of
5) Tuymazy mazout
6) Baku mazout
7) Bugul'ma petroleum.

The surface tension of liquid boiler fuels drops linearly with rising temperature. Usually, viscous mazouts have higher surface tension (Fig. 4.16) than low-viscosity types (Table 4.38).

Pour Point

The pour points of mazouts depend on the chemical nature of the raw material, the degree of removal of light fractions from the raw material, and the production process (direct distillation or cracking). The pour points of straight-run mazouts from paraffin-base petroleum are usually considerably higher than those of mazouts from naphthenoaromatic petroleums. Increased degrees of refinement of the raw material raise mazout pour points markedly (Table 4.39).

The pour points of fleet mazouts, according to AUSS specifications, may not exceed minus 5 to minus 8°C, and those of firebox mazouts 10-36°C. We encounter fleet mazouts with pour points as low as -30°C, firebox grades up to +42°C and above (paraffin-base), and high-viscosity cracking mazouts with pour points from 25 to 34°C.

The pour points of mazouts as determined by the standard method (preheating to +50°C) may differ sharply from the actual pour points of these products under operating conditions; this is explained by a change in pour point as a function of heat-treatment conditions, i.e., on the temperature and duration of heating and the cooling rate. Usually, the maximum pour points of mazouts are observed on heating from 30 to 70°C, and the minimal values on heating from 80 to 100°C (Table 4.40). A further increase in the heating temperature to 130-150°C has no influence on pour point. The -28°C mazout pour point established according to the AUSS and below does not change on heat treatment. The kinetics of variation of the pour points of various mazouts during heating can be traced in Figs. 4.17-4.19. An increase in the time of preheating (over and above the heating time set by the AUSS) results in a sharp decrease in pour point (Table 4.41).

TABLE 4.39

Variation of Pour Point as a Function of Degree of Refinement and Viscosity of Mazouts

1 Нефть	2 Способ переработки	3 Условная вязкость при 50° C, °ВУ	4 Температура застывания, °C (ГОСТ 1533—42)
5 Туймазинская	6 Прямая перегонка	4,38	—14
7 Эхабинская	8 То же	5,59	—8
	»	?,8	+3
	»	?2	—21
	»	80	+22
9 Смесь ишимбайской и туймазинской	»	7,78	+13
	»	40	+40
10 Смесь ставропольской и бавлинской	11 Крекинг	9,26	—10
	»	12,1	—6
	»	14,1	—4
	»	19	+2

1) Petroleum
2) Refining process
3) Conventional viscosity at 50°C, °VC
4) Pour point, °C (AUSS 1533-42)
5) Tuymazy
6) Direct distillation
7) Ekhabi
8) Same
9) Mixture of Ishimbay and Tuymazy
10) Mixture of Stavropol' and Bavly
11) Cracking.

TABLE 4.40

Guideline Heating Temperatures for Mazouts to Obtain Maximum and Minimum Pour Points

1 Топливо	Температура нагрева мазутов (в °С) для получения температуры застывания 2	
	3 максимальной	4 минимальной
5 Парафинистые мазуты	60—70	80—100
6 Топочные крекинг-мазуты	20—30	80—100
7 Флотские мазуты:		
8 малосернистые прямой перегонки	50—60	70—90
9 сернистые прямой перегонки	40—50	70—90
10 сернистые крекинг-мазуты	20—30	90—100

1) Fuel
2) Heating temperature of mazouts (°C) to make pour point
3) Maximal
4) Minimal
5) Paraffin-base mazouts
6) Firebox cracking mazouts
7) Fleet mazouts
8) Straight-run low-sulfur
9) Straight-run sulfur-containing
10) Sulfur-containing cracking mazouts.

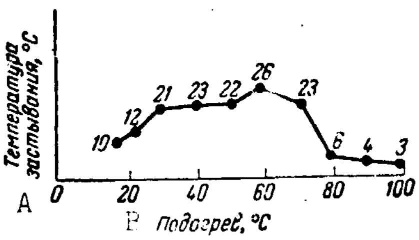

Fig. 4.17. Pour point of Groznyy paraffin-base mazout as a function of preliminary heat treatment. The numerals on the lines indicate the pour point of the mazout. A) Pour point, °C; B) warming, °C.

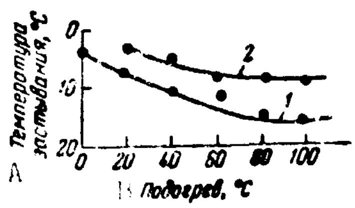

Fig. 4.18. Pour points of cracking mazouts as functions of preliminary heat treatment: 1) Groznyy, VC_{50} = 36; 2) Tuapse, VC_{50} = 77. A) Pour point, °C; B) warming, °C.

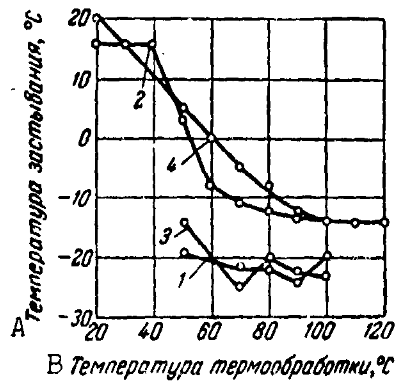

Fig. 4.19. Pour points of fleet mazouts as functions of prior heating temperature: 1) low-sulfur mazout, VC_{50} = 12 (pour point -19°C); 2) sulfur-containing cracking mazout, VC_{50} = 12 (pour point +3°C); 3) straight-run sulfur-containing mazout, VC_{50} = = 4.38 (pour point -14°C); 4) sulfur-containing cracking mazout, VC_{50} = 12.8 (pour point +5°C). A) Pour point, °C; B) heat treatment temperature, °C.

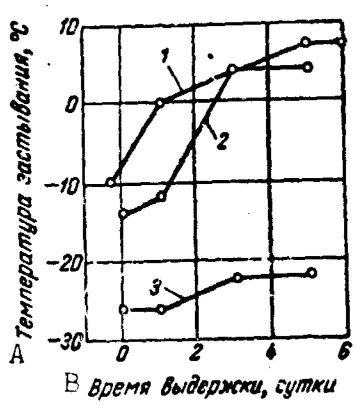

Fig. 4.20. Variation of mazout pour points in time: 1) sulfur-containing cracking mazout (pour point +5°C) treated for 30 min at 70°C; 2) same, for 2 h; 3) low-sulfur F12 mazout (pour point -22°C) treated for 2 h at 70°C. A) Pour point, °C; B) holding time, days.

The pour point of mazout is unstable after heat treatment (70-100°C) and returns to its original value during subsequent storage (Fig. 4.20).

TABLE 4.41

Influence of Heat Treatment Time at 70°C on Pour Point

A Мазут	B Температура застывания °С (по ГОСТ 1533–42)	C Температура застывания после термообработки в течение D 2 ч	6 ч
E Сернистый крекинг-мазут Ф12	−6	−14	−20
	−9	−12	−25
	−5	−9	−23
F Сернистый крекинг-мазут 20	+4	−1	−8
G Малосернистый Ф12	−18	−20	−26
	−20	−28	−30
	−19	−28	−28
	−30	−30	−30

A) Mazout
B) Pour point, °C (AUSS 1533-42)
C) Pour point after heat treatment for
D) 2 hours
E) Sulfur-containing F12 cracking mazout
F) Sulfur-containing No. 20 cracking mazout
G) Low-sulfur F12.

Flash Point

The flash point of a liquid boiler fuel is an indicator that permits inferences as to the fire hazard that it represents. This indicator becomes particularly important for fuels used in shipboard installations, where they are stored near crew's quarters and boiler rooms. Hence the flash points of fleet mazouts are determined in a close crucible, and those of firebox mazouts in an open crucible. When determined in a closed device, the flash point is usually found to be lower (by as much as 30°C) than that for an open device.

TABLE 4.42

Flash Points of Boiler Fuels

A Топливо	B Метод получения	C Температура вспышки (в °C) определенная в D закрытом тигле	E открытом тигле	F Разница между определениями, °C
G Мазут флотский Ф12	H Прямой перегонки	100	112	12
	I То же	94	112	18
	J Крекинг	75	140	65
	I То же	84	146	62
K Мазут топочный:				
L $ВУ_{80}$ = 20	H Прямой перегонки	98	132	34
40	I То же	106	164	58
40	J Крекинг	76	138	62
M Сланцевый мазут	N Коксование	109	121	12
O Ярегская нефть	—	104	112	8

A) Fuel
B) Method of production
C) Flash point (°C) determined in
D) Closed crucible
E) Open crucible
F) Difference between determinations, °C
G) F12 fleet mazouts
H) Direct distillation
I) Same
J) Cracking
K) Firebox mazout
L) VC_{50} = 20
M) Shale mazout
N) Coking
O) Yarega petroleum.

TABLE 4.43

Change in Flash Point of Cracking Mazout during Shipment in Tank Cars

1 Температура вспышки, °C				1 Температура вспышки, °C			
2 Данные завода, средняя проба	3 данные потребителя			2 Данные завода, средняя проба	3 данные потребителя		
	4 верх	5 середина	6 низ		4 верх	5 середина	6 низ
75	86	86	85	81	88	94	92
78	86	87	86	75	100	91	98
81	92	90	92	79	98	97	95
80	90	94	95				

1) Flash point, °C
2) Refinery data, average sample
3) Customer's data
4) Top
5) Middle
6) Bottom.

TABLE 4.44

Change in Flash Point on Heating

1 Метод получения мазута	2 Вязкость условная при 50° C, °ВУ	3 Температура вспышки до подогрева, °C	4 Температура вспышки при подогреве до				6 Температура вспышки, °C, без перемешивания 12 ч
			75° C		90° C		
			5 время термообработки, мин				
			60	10	30	60	
7 Крекинг	12	96	117	102	—	117	114
	40	76	100	76	88	100	94
8 Прямая перегонка	4,58	88	104	94	104	104	102
	12	98	102	102	—	108	102

1) Method of producing mazout
2) Conventional viscosity at 50°C, °VC
3) Flash point before preheating, °C
4) Flash point on warming to
5) Heat-treatment time, min
6) Flash point, °C, without agitation, 12 h
7) Cracking
8) Direct distillation

Cracking mazouts, and especially the low-viscosity grades, frequently have lower closed-crucible flash points as a result of their content of volatile decomposition products, which dissipate in an open device before enough of them have accumulated for deflagration, and hence the difference between the determinations ranges up to 70°C (Table 4.42). During shipment and storage, the flash points of these mazout grades usually rise (Table 4.43). When cracking mazouts are heated, the flash point also rises, but only to a certain limit, after which even prolonged warming does not affect flash point (Table 4.44).

Under the conditions of storage in tanks, the flash points of mazouts are usually slightly higher than the temperature determined by the standard method [18] and depend on tank volume and the level of the liquid. Thus, when mazouts are warmed in open (unpressurized) vessels, their temperatures must be 10-20°C below their flash points. In closed containers under pressure (oil preheaters, coils, piping), mazout can be warmed to a temperature above its flash point.

Fractional Composition

The fractional composition of mazouts used as boiler fuels is not regulated and not determined. Low-viscosity (light) mazouts contain more of the light fractions than do the viscous (heavy)

TABLE 4.45

Fractional Compositions of Low-Viscosity Mazouts [5]

1 Показатели	2 Малосернистый мазут Ф12	3 Сернистый мазут	
		4 прямой перегонки Ф5	5 крекинг Ф12
6 Фракционный состав:*			
7 начало кипения, °C	267	225	257
8 перегоняется при °C:			
10%	313	254	300
20%	330	287	335
30%	348	322	350
40%	352	346	345
50%	—	358	360
9 Начало разложения, °C	357	358	—
10 Температура вспышки, °C	102	94	84

*In % by volume.

1) Index
2) F12 low-sulfur mazout
3) Sulfur-containing mazout
4) Straight-run F5
5) F12 cracking
6) Fractional composition
7) Start of boiling
8) Distilled over at ... °C
9) Start of decomposition, °C
10) Flash point, °C.

mazouts. Low-viscosity [illegible] of the fleet types contain 20% and more of the diesel-fue[illegible]ns boiling below 330°C (Table 4.45). Viscous mazouts (heav[illegible]) have higher boiling points than the low-viscosity gr[illegible] contain more of the high-boiling

fractions. The heaviest mazouts — high-viscosity cracking residues -- generally have initial boiling temperatures of 300°C and above; on the average, 8-12% boils out below 350°C [3].

Increased contents of high-boiling fractions are detrimental to completeness of combustion and increase the amount of smoke and soot formed. Combustion of fuels with high contents of light distillates in fireboxes that are not adapted for such fuels also has its effect on the combustion process. The depth of penetration of the flame is reduced. The lighter part of the fuel, burning in the front of the firebox, may cause local overheating, buckling and deformation of the boiler tubes. The heavy particles of the fuel, thrown into the interior of the firebox, burn with inadequate air, with the result that more smoke and more soot deposits on the lining and working surfaces of the boiler are formed.

Mechanical Impurities in the Fuel

The mechanical impurities in mazouts consist of minute particles of iron, sand, coked carbon deposits, packing and gasket fibers, etc. They clog filters, nozzles and valves and cause wear of

TABLE 4.46

Influence of Solvents on Content of Mechanical Impurities in Mazouts

1 Топливо	2 Содержание механических примесей (в %) после промывки			6 Содержание несгораемых примесей (в %) после промывки	
	3 бензином	4 бензолом	5 хлороформом	4 бензолом	5 хлороформом
7 Крекинг-мазут Ф12	0,9750	0,0844	0,0220	0,0201	0,0174
8 Топочный крекинг-мазут 40	3,3030	0,5778	0,3478	0,0158	0,0084

1) Fuel
2) Content of mechanical impurities (%) after scrubbing with
3) Benzine
4) Benzene
5) Chloroform
6) Content of noncombustible impurities (%) after scrubbing with
7) F12 cracking mazout
8) No. 40 firebox cracking mazout.

the walls of passages in nozzles and nozzle heads, thereby interfering with the fuel-atomizing process. Nozzle wear is more rapid when high-viscosity cracking mazouts containing up to 2.5% mechanical impurities are used than when low-viscosity fleet mazouts containing up to 0.1% of mechanical impurities are employed. In determination of mechanical impurities according to AUSS 6370-59, the asphalt-tar substances present in the mazouts, which are settled out simultaneously, are often determined along with them. In

this case, the stated mechanical impurity content will be on the high side, and the true amount can be determined by using various solvents to wash the precipitated impurities (Table 4.46).

Tar Constituents

The tar constituents present in boiler fuels are detrimental to fuel properties and complicate use conditions. Loss of stability of the mazouts, disturbances in the process of burning them,

TABLE 4.47

Average Content (%) of Tar Constituents in Mazouts

1 Мазуты	2 Смолы	3 Асфальтены	4 Карбены и карбоиды	5 Акцизные смолы	6 Коксуемость
7 Крекинг-мазут Ф12	10,59	4,3	0,19	40	10,22
8 Крекинг-мазут 40	8,12	6,64	1,32	72	15,2
9 Сернистый мазут прямой перегонки Ф5	13,6	0,94	0,03	28	[illegible],97
10 Малосернистый мазут прямой перегонки Ф12	14,03	0,11	0,03	28	5,79
11 Топочный 200 (крекинг-остаток) [3]	16,6	14,5	1,19	—	17,6

1) Mazout
2) Tars
3) Asphaltenes
4) Carbenes and carboids
5) "Excise" tars
6) Coking capacity
7) F12 cracking mazout
8) No. 40 cracking mazout
9) Straight-run F5 sulfur-containing mazout
10) Straight-run F12 low-sulfur mazout
11) No. 200 firebox mazout (cracking residue) [3].

and the formation of emulsions with water are associated with the presence of tars in mazouts. The tar constituents are regulated only for fleet mazouts; their contents are determined by "excise" tars (Table 4.47).

Cracking mazouts differ from straight-run types in having higher contents of "excise" tars; here, the higher the viscosity of the mazout, the greater the tar content. The tars, asphaltenes, carbenes and carboids present in mazouts affect their properties in different ways, with the asphaltenes being most detrimental. The asphaltene content of the fuel can be judged from its coking capacity; the higher this index, the greater the asphaltene content. Coking capacity characterizes the total tar content more accurately than does the content of "excise" tars. Cracking mazouts also differ from straight-run grades in having a higher content of asphaltenes, carbenes and carboids (see Table 4.47). In heavy high-viscosity cracking mazouts, their content ranges up to 14-20% (Table 4.48).

Fuels with a high content of tar constituents are usually unstable, and tarry deposits form in storage and on heating; these may include mechanical impurities, water, extracted oil and solid

TABLE 4.48

Content of Asphaltenes, Carbenes and Carboids in Cracking Mazouts

A Мазуты	B Условная вязкость °ВУ	C Содержание асфальтенов (А), %	D Содержание карбенов и карбоидов ($К_1+К_2$), %	E Содержание $А+К_1+К_2$, %
1. Крекинг-мазут 40	38 (50° C)	7,42	0,98	8,40
2. То же 60	9,4 (80° C)	11,70	2,60	14,30
3. То же 80	22,2 (75° C)	9,36	1,90	11,26
4. Крекинг-остаток Одесского завода	120 (50° C)	11,32	0,90	12,22
5. То же	380 (50° C)	14,11	2,30	16,41
6. »	18,4 (80° C)	14,80	1,79	16,59
7. »	100 (50° C)	19,10	2,00	21,00

Note. 1, 2, and 3 are data of ОНИМФ; 4, 5, 6 and 7 are data of the Odessa refinery laboratory [19].

A) Mazout
B) Conventional viscosity, °VC
C) Asphaltene content (A), %
D) Carbine and carboid content ...
E) Content of ...

1. No. 40 cracking mazout
2. Same, No. 60
3. Same, No. 80
4. Odessa refinery cracking residue
5. Same.

TABLE 4.49

Composition of Sludge (%) from Oil Preheaters

1 Пробы для определения содержания отложений	2 Смолы	3 Асфальтены	4 Карбены и карбоиды	5 Масла	6 Механические примеси
7 В нефтеподогревателе	5,93	3,26	1,57	34,83	59,48
8 В пересчете на мазут, за исключением механических примесей	13,01	7,15	3,45	76,37	—

1) Sample for determination of sludge content
2) Tars
3) Asphaltenes
4) Carbenes and carboids
5) Oils
6) Mechanical impurities
7) In oil preheater
8) Converted to mazout, excepting mechanical impurities.

paraffins. In storage of boiler fuels and with periodic warming, tarry deposits are precipitated comparatively quickly. At 120°C, [illegible]% of the carbenes and carboids settle within 5 h, and up to 97% during 22 h at 250°C [20].

TABLE 4.48

Content of Asphaltenes, Carbenes and Carboids in Cracking Mazouts

A Мазуты	B Условная вязкость °ВУ	C Содержание асфальтенов (А), %	D Содержание карбенов и карбоидов ($К_1+К_2$), %	E Содержание $А+К_1+К_2$, %
1. Крекинг-мазут 40	38 (50° C)	7,42	0,98	8,40
2. То же 60	9,4 (80° C)	11,70	2,60	14,30
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Note. 1, 2, and 3 are data of ОНИМФ; 4, 5, 6 and 7 are data of the Odessa refinery laboratory [19].

A) Mazout
B) Conventional viscosity, °VC
C) Asphaltene content (A), %
D) Carbine and carboid content ...
E) Content of ...

1. No. 40 cracking mazout
2. Same, No. 60
3. Same, No. 80
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5. Same.

TABLE 4.49

Composition of Sludge (%) from Oil Preheaters

1 Пробы для определения содержания отложений	2 Смолы	3 Асфальтены	4 Карбены и карбоиды	5 Масла	6 Механические примеси
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1) Sample for determination of sludge content
2) Tars
3) Asphaltenes
4) Carbenes and carboids
5) Oils
6) Mechanical impurities
7) In oil preheater
8) Converted to mazout, excepting mechanical impurities.

paraffins. In storage of boiler fuels and with periodic warming, tarry deposits are precipitated comparatively quickly. At 120°C, 23.6% of the carbenes and carboids settle within 5 h, and up to 97% during 22 h at 250°C [20].

to 20-30%, depending on the temperatures of the mazout and the air, the viscosity of the mazout, and the steam temperature and pressure. The watering of mazout washings caught during thorough cleaning of railroad tank cars, oil barges and tanks to remove residues ranges [24] up to 50-75%. When hot water is used for washing with a hydraulic monitor, the mazout may be watered up to 80% [25].

When water is mixed with mazout, the result is a hydrophobic emulsion of the "water in oil" type. The more highly the emulsion is dispersed, the more stable it becomes. In turn, the dispersion of the emulsion depends on the viscosity and density of the mazout, the thoroughness of mingling of the water with it, and the amount and nature of emulsion stabilizers (emulsifiers).

The emulsion formed when low-viscosity mazouts are mixed with water is usually broken down comparatively easily by warming it and allowing it to stand. In this case, the settling of the water depends on the density of the mazout. The lighter the mazout, the more rapidly will the water separate out from it. Figures 4.21 and 4.22 show the variation of the densities of water, light mazouts and cracking residues as functions of temperature.

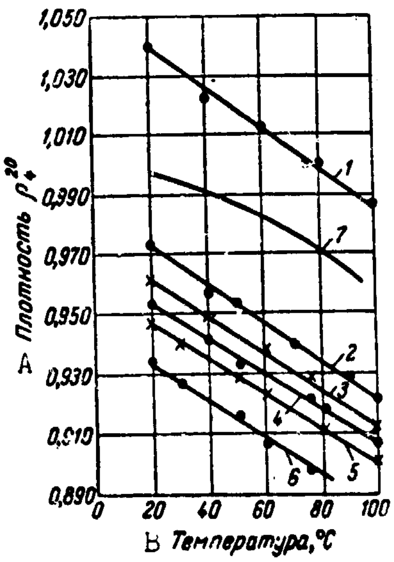


Fig. 4.21. Density of low-viscosity mazouts as a function of temperature: 1) shale mazout, VC_{50} = 22; 2) firebox mazout, VC_{50} = 20; 3, 4, 5, 6) fleet mazouts, VC_{50} = 20; VC_{50} = 15.6; VC_{50} = 12; VC_{50} = 5; 7) water. A) Density; B) temperature, °C.

TABLE 4.50

Effectiveness of Deemulsifiers*

1 Деэмульгатор	2 Содержание деэмульгатора, %	3 Время отстоя, ч	4 Количество отстоявшейся воды, %	5 Количество воды в мазуте после отстоя в нижнем слое, %
6 Без деэмульгатора . . .	—	48	—	16,0
7 ОП-7	0,1	34	61	1,8
	0,25	16	85	0,73
	0,5	4	85	0,7
8 Щелочные отходы	0,25	36	44	2,6
	0,5	36	88	0,6

*Settling at 70°C, water content in emulsion 10-12%.

1) Deemulsifier
2) Deemulsifier content, %
3) Standing time, h
4) Amount of water separated, %
5) Amount of water in mazout after standing, in bottom layer, %
6) Without deemulsifier
7) OP-7
8) Alkali wastes.

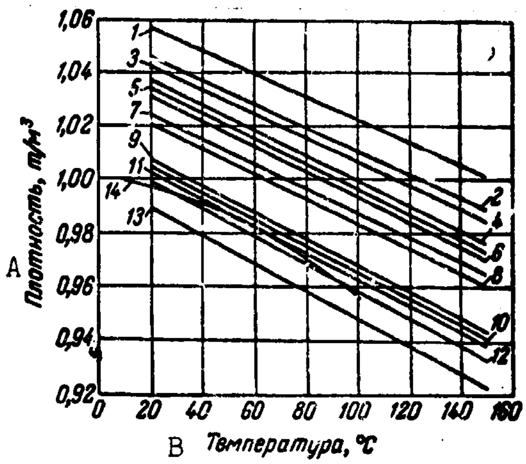


Fig. 4.22. Change in density of cracking residues, mazouts and water as a function of temperature: 1, 3, 4, 5, 6, 11) Tuymazy mazout with 20°C density of, respectively, 1.058, 1.044, 1.036, 1.034, 1.031, 1.004; 2, 7, 8, 9, 10) Baku mazout with 20°C densities of, respectively, 1.046, 1.026, 1.022, 1.006, 1.005; 12) Bugul'ma petroleum with 20°C density of 1.0; 13) Nos. 80 and 100 mazout; 14) water. A) Density, tons/m³; B) temperature, °C.

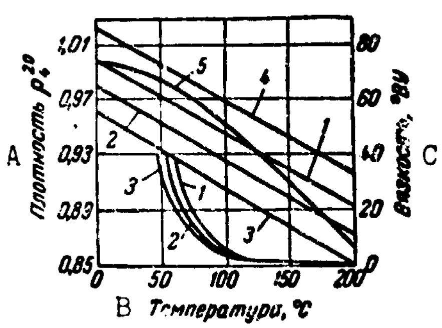


Fig. 4.23. Viscosity and density of various mazout grades and water as functions of temperature [21]: 1, 2, 3, 4) Nos. 80, 60, 40 and 100 mazouts, respectively; 5) water. A) Density; B) temperature, °C; C) viscosity, °VC.

Emulsions obtained by warming mazouts with live steam are more stable than those formed by mixing water and mazout. In this case, the persistence of the emulsion depends on the amount and effectiveness of emulsion stabilizers present in the mazouts. The stabilizers of water-mazout emulsions are chiefly asphaltenes and some of the tars [22]. In emulsions of sulfur-containing mazouts (especially cracking mazouts), the degree of water-droplet dispersion is substantially higher than in low-sulfur mazouts and, con-

sequently, the persistence of the emulsions will be considerably greater.

To separate water from the mazout, it is usually heated to 40-70°C and then allowed to stand for a long period. Mazouts obtained from nonsulfurous petroleums (especially low-viscosity grades) separate quite readily from water, while stable emulsions form in sulfur-containing mazouts because of their higher asphaltene contents and are difficult to separate by ordinary settling and heating. In sulfur-containing cracking mazouts, the emulsion is almost permanent and the water does not separate. Water separation is particularly poor in high-viscosity firebox mazouts.

At high temperatures (110-160°C), when high-viscosity mazouts have their lowest and practically constant viscosity, separation of water is inhibited by the very small difference between the water and mazout densities, and at temperatures below 100°C, water fails to separate because of the high viscosity of the mazouts (Fig. 4.23). As a result, the rate of separation of water droplets from low-viscosity mazouts is considerably higher for identical temperature conditions than the rate of separation from high-viscosity grades. The rate of water separation varies with temperature.

Water is removed most effectively from Nos. 40 and 60 firebox mazouts in the 110-140°C temperature range, and from Nos. 80 and 100 mazouts at about 210°C. Here the water must be allowed to settle out under high pressure (up to 25 atm for No. 100 mazout) [25].

One of the most effective methods of dealing with emulsions is to use deemulsifiers [26]. OZhK, VNII NP-58, proxalines, proxanols, and others are recommended as deemulsifiers for firebox mazouts [27-29].

Active deemulsifiers for low-viscosity mazouts include hydroxyethylated phenols OP-7 and OP-10 (TU 3554-53) and sodium salts of sulfo acids (alkali wastes formed in acid-alkali scrubbing of oily petroleum distillates, TU 330-48). The efficiencies of deemulsifiers are given in Tables 4.50 and 4.51 [34].

TABLE 4.51

Influence of OP-7 Deemulsifier on Strength of Film and Surface Tension of Straight-Run Sulfur-Containing Mazout

1 Продукты	2 Содержание деэмульгатора в мазуте, %	3 Поверхностное натяжение, эрг/см²	4 Прочность (продолжительность) пленки, [illegible]
5 Мазут без деэмульгатора	—	26,5	8,5
6 Мазут с деэмульгатором ОП-7	0.10	10,7	—
	0,25	8,5	5,0
	0,50	4,7	2,3
	1,00	1,8	1,4

1) Product
2) Deemulsifier content in mazout, %
3) Surface tension, ergs/cm²
4) Strength (persistence) of film, s
5) Mazout without deemulsifier
6) Mazout with OP-7 deemulsifier.

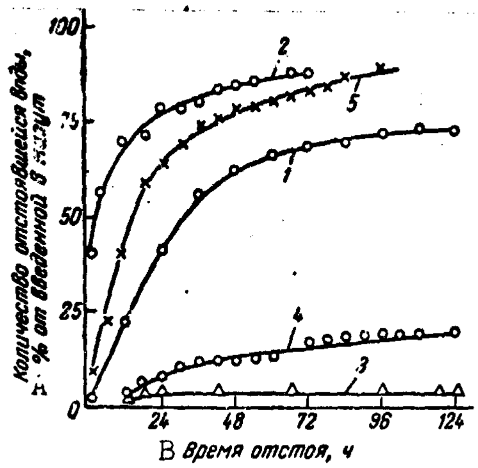


Fig. 4.24. Separation of water from mazouts in the railroad tank car. Mazout F12: 1) settling without heating; 2) settling with heating to 60°C; sulfur-containing FS5 mazout: 3) settling without heating; 4) settling with heating to 60°C; 5) settling with 0.25% of OP-7 deemulsifier and heating to 60°C. A) Amount of water separated, % of water introduced into mazout; B) settling time, h.

A test of OP-7 deemulsifier under industrial conditions (0.25% OP-7 concentration, standing at 60°C) has confirmed its high quality (Fig. 4.24). It is recommended that deemulsifiers be introduced into the mazouts before they become watered and form emulsions, i.e., at the points of production, since their effectiveness is then higher than when they are added to emulsion.

In laboratory practice, the effectiveness of deemulsifiers can be evaluated by two indices: 1) the strength of bubble films (from their lifetimes); 2) the decrease in surface tension (see Table 4.51). Pluronic L-62, 4411, and Teepol are regarded as the best of the imported deemulsifiers.

Recently, heavily watered high-viscosity mazouts and mazout rinsings have come into use as boiler fuels for stationary boilers without preliminary dewatering; this is made possible by formation of a water-mazout emulsion with the water (up to 30%) uniformly distributed through the entire volume of the fuel by means of a high-speed mechanical disperser or by direct bubbling of live steam or compressed air through the mazout [24]. When the water content in the emulsion is over 30%, combustion deteriorates markedly and the boiler's efficiency and steam output fall.

Ash Content in Fuel. Vanadium Corrosion

Liquid boiler fuels usually contain from 0.01 to 0.5% ash. This is formed chiefly by metal salts. Salts may be present in the petroleum in dissolved form (chemically bound salts) or in the colloidal state (complex compounds of metals); they may also enter it together with the drilling waters.

TABLE 4.52

Relation Between Content of Asphalt-Tar Constituents, Sulfur and Vanadium in Petroleums [5]

1 Содержание серы в нефтях, %	2 Средняя плотность ρ_4^{20}	3 Среднее содержание, %			7 Среднее содержание, мг на 100 г нефти	
		4 серы	5 смол	6 асфальтенов	8 порфиринов	9 ванадия
10 До 0,3	0,863	0,24	5,2	1,8	11 Следы	0,04
0,3—0,7	0,916	0,44	9,8	2,9	1,53	0,58
0,7—2,0	0,860	1,32	6,1	3,8	18,90	3,28
2,0—3,0	0,878	2,42	8,0	1,8	30,00	7,29
12 Более 3,0	0,906	3,70	12,0	7,4	81,70	13,57

1) Sulfur content in petroleums, %
2) Average density
3) Average contents
4) Sulfur
5) Tars
6) Asphaltenes
7) Average content, mg per 100 g of petroleum
8) Porphyrins
9) Vanadium
10) Up to
11) Traces
12) More than.

More than 25 elements are encountered in the ash left by combustion of petroleum. The basic components are iron, vanadium, nickel, aluminum, calcium and sodium. Compounds of vanadium and sodium cause corrosion of the metallic surfaces of boilers and gas-turbine plants. All vanadium compounds concentrate in the asphalt-tar fractions of the petroleum, chiefly among the asphaltenes.

The vanadium contents of petroleums increase in the following order:

paraffinic → naphthenic → aromatic →
→ high-tar → asphaltene petroleums

The vanadium content in petroleum depends on its sulfur content (Table 4.52). Low-tar and low-sulfur petroleums from the Azerbaydzhan SSR, such as Balakhany, Kara-Chukhur, Buzovna, and other petroleums, contain about $6 \cdot 10^{-5}$% vanadium; Groznyy petroleums contain $(2\text{-}8) \cdot 10^{-3}$%, and Turkmenian petroleums $(2\text{-}3) \cdot 10^{-2}$%. In sulfur-containing petroleums from the eastern deposits, the vanadium content is substantially higher, reaching $1 \cdot 10^{-2}$%, and

averaging $(5\text{-}6) \cdot 10^{-3}$. Table 4.53 lists vanadium contents for certain individual petroleums.

Detailed analyses of ashes from various mazouts has shown that the ashes of sulfur-containing and low-sulfur mazouts have closely similar compositions (Table 4.54). The basic difference observed in sulfur-mazout ash consists in the presence of vanadium, which is absent for low-sulfur mazouts or present in negligible quantities, and in elevated sodium content. In F12 fleet mazout obtained from nonsulfurous petroleums, there is no more than 0.0005% of vanadium. Straight-run sulfur-containing fleet mazout contains up to 0.003-0.007% vanadium; the content ranges to 0.01% in sulfur-containing cracking mazouts [5], to 0.007% in No. 20 firebox mazout, to 0.012% in Nos. 40, 60 and 80 mazouts, and to 0.020% in cracking residues [30].

The vanadium contents of mazouts obtained from certain foreign petroleums are given in Table 4.55.

TABLE 4.53

Vanadium Contents of Certain Individual Petroleums of the Soviet Union

1 Нефти	2 Зола, %	3 V_2O_5 на золу, %	4 Ванадий, мг, на 100 г нефти	5 Примечание
6 Сураханская легкая		0,64		7 По данным Добрянского
8 Балаханская тяжелая		0,07		
9 Косчагыльская		0,44		
10 Чусовская		7,54		
11 Краснокамская		7,17		
12 Ишимбаевская		17—51		
13 Туймазинская		20—35		
14 Старогрозненская			0,51	15 По данным Деменковой и Курбацкой
16 Октябрьская			0,044	
17 Ташкалинская			0,03	
18 Небит-Дагская			0,023	
19 Жигулевская			3,52	
20 Сызранская			6,37	
21 Ромашкинская			4,18	
22 Бавлинская			2,65	
23 Туймазинская Д			2,4	
24 То же, C_1			10,55	
25 Краснокамская			1,56	
26 Северокамская			0,868	
27 Зиневская	1,94	5,6	61,0	28 По данным Л. А. Гуляевой
29 Бугурусланская P_2	0,0297	65,33	10,8	
30 Ишимбайская, западный массив, P_1	0,0181	31,35	3,18	
31 Краснокамская C_2 (Мартьян)	0,0114	30,47	1,94	
32 Северокамская C_2 (Мартьян)	0,0044	35,21	0,868	
33 Сызранская (верейский горизонт) C_2	0,0237	42,23	5,6	
34 Туймазинская C_1	0,0355	63,60	12,7	
»	0,0234	64,01	8,39	

1) Petroleum
2) Ash, %
3) V_2O_5 on ash, %
4) Vanadium, mg per 100 g of petroleum
5) Remarks
6) Surakhany light
7) According to Dobryanskiy
8) Balakhany heavy
9) Koschagyl
10) Chusovoy
11) Krasnokomsk
12) Ishimbay
13) Tuymazy
14) Starogroznyy
15) According to Demenkova and Kurbatskaya

16) Oktyabr'
17) Tashkala
18) Nebit-Dag
19) Zhigulevsk
20) Syzrany
21) Romashkiny
22) Bavly
23) Tuymazy D
24) Same, S_1
25) Krasnokamsk
26) Severokamsk
27) Zmiyev
28) According to L.A. Gulyayeva
29) Bugurusian R_2
30) Ishimbay, west massif, R_1
31) Krasnokamsk S_2 (Mart'yan)
32) Severokamsk S_2 (Mart'yan)
33) Syzrany (gate level) S_2
34) Tuymazy S_1.

TABLE 4.54

Composition of Ash from Sulfur-Containing and Low-Sulfur Mazouts [54]

1 Показатели	2 Сернистый крекинг-мазут из смеси ставропольской, саратовской и бавлинской нефтей	3 Сернистый прямогонный мазут из туймазинской нефти	4 Флотский мазут из ильской нефти
5 Сера, %	2,2	1,8	0,8
6 Зола, %	0,183	0,076	0,106
7 Анионы и катионы в минеральной части мазутов, %:			
Cl	2,19	8,17	6,32
SO_4	20,39	28,33	26,18
Na	1,91	3,03	8 Отсутствие
Ca	16,11	27,93	27,62
Mg	2,50	6,73	5,55
Ni	0,74	1,05	4,28
Mn	9 Следы	9 Следы	0,06
Fe	1,04	8,71	14,44
Al	8,68	9,62	6,64
V	0,61	1,92	Следы
SiO_2	45,63	4,46	9,09
10 Окислы в золе мазута, %:			
Na_2O	3,09	5,66	8 Отсутствие
CaO	9,31	20,51	20,43
MgO	5,20	16,25	12,92
Fe_2O_3	1,87	18,05	29,01
Al_2O_3	20,42	26,27	17,00
NiO	1,18	1,93	7,65
MnO	9 Следы	9 Следы	0,12
V_2O_5	1,38	4,98	9 Следы
SiO_2	57,35	6,45	12,77

1) Index
2) Sulfur-containing cracking mazout from mixture of Stavropol', Saratov and Bavly petroleums
3) Sulfur-containing straight-run mazout from Tuymazy petroleum
4) Fleet mazout from Il'skiy petroleum
5) Sulfur
6) Ash
7) Anions and cations in mineral part of mazout
8) None
9) Traces
10) Oxides in mazout ash.

TABLE 4.55

Vanadium Contents in Mazouts from Foreign Petroleums [31]

1 Происхождение мазутов	2 Выход мазута, % на нефть	3 Зола, % на мазут	4 Содержание ванадия, % на золу
5 Венесуэла	58,0	0,115	40,7
6 Иран	45,0	0,0503	18,3
7 Ирак	32,5	0,0168	57,5
8 Саудовская Аравия	17,8	0,0148	15,3
7 Ирак	45,8	0,0303	17,4

1) Origin of mazout
2) Mazout yield, % on petroleum
3) Ash, % on mazout
4) Vanadium content, % on ash
5) Venezuela
6) Iran
7) Iraq
8) Saudi Arabia.

Despite the relatively low ash content in boiler fuel, ash deposits form on boiler heating surfaces and the in-stream parts of gas turbines when it is burned, lowering the operating reliability and technical-economic performance of these machines: heat-transfer conditions suffer, the exhaust-gas temperature rises, and, as a consequence, the power and efficiency of the boiler or gas turbine [GT] (ГТУ) decrease. Furthermore, ash deposits intensify the corrosion of metallic surfaces and damage boiler linings. The growth of deposits is accelerated noticeably in the presence of sulfur [32].

Table 4.56 lists compounds that may form during combustion of mazouts and their melting points [33].

Table 4.57 shows the composition of firebox-mazout ashes and deposits from gas-turbine machinery [35]. In this case, the deposits on the guide vanes and buckets have about the same composition as the mazout ash (with the exception of the alkaline-earth metal oxides).

Table 4.58 gives an analysis of deposits [34] taken from the heating surfaces of a boiler installation after operation on sulfur-containing and low-sulfur mazouts. The main components of the deposits are identical to the mazout-ash components.

The main content of deposits taken fro the regenerative air preheater is iron. Typical of all deposits is the absence of chlorides, despite the fact that the mineral impurities of the mazouts contained large quantities of them. For the most part, the deposits consist of sulfates. The basic difference between the compositions of sulfur-containing- and nonsulfurous-mazout deposits consists in the former's containing vanadium and more insoluble oxides, which interfere with cleaning. Deposits form more rapidly and in larger quantities during combustion of sulfur-containing mazouts than during combustion of low-sulfur grades, and are

TABLE 4.56

Melting Points of Compounds Formed on Combustion of Mazouts

1 Соединение	2 Формула	3 Температура плавления, °C	4 Возможные реакции соединения, °C
5 Окись алюминия . .	Al_2O_3	2050	—
6 Сульфат алюминия	$Al_2(SO_4)_3$	—	7 700° C в Al_2O_3
8 Окись кальция . . .	CaO	2572	—
9 Сульфат кальция . .	$CaSO_4$	1450	—
10 Окись железа	Fe_2O_3	1565	—
11 Сульфат железа . . .	$Fe_2(SO_4)_3$	—	480° C в Fe_2O_3
12 Окись магния	MgO	2500	—
13 Сульфат магния . . .	$MgSO_4$	—	1124° C в MgO
14 Окись никеля	NiO	2090	—
15 Сульфат никеля . . .	$NiSO_4$	—	480° C в NiO
16 Окись кремния . . .	SiO_2	1720	—
17 Сульфат натрия . . .	Na_2SO_4	880	—
18 Бисульфат натрия . .	$NaHSO_4$	—	250° C в $Na_2S_2O_7+H_2O$ 460° C в $Na_2SO_4+SO_3$
19 Пиросульфат натрия	$Na_2S_2O_7$	400	—
20 Трехокись ванадия	V_2O_3	1970	—
21 Четырехокись ванадия	V_2O_4	1970	
22 Пятиокись ванадия	V_2O_5	675—690	—
23 Окись цинка	ZnO	1800	
24 Сульфат цинка . . .	$ZnSO_4$	—	740° C в ZnO
25 Метаванадат натрия	$Na_2O \cdot V_2O_5$	630	—
26 Пированадат натрия	$2Na_2O \cdot V_2O_5$	640	—
27 Ортованадат натрия	$3Na_2O \cdot V_2O_5$	850	—
28 Пированадат никеля	$2NiO \cdot V_2O_5$	900	—
29 Ортованадат никеля	$3NiO \cdot V_2O_5$	900	—
30 Метаванадат железа	$Fe_2O_3 \cdot V_2O_5$	860	—
31 Ванадат железа . . .	$Fe_2O_3 \cdot 2V_2O_5$	855	
32 Ванадил ванадат натрия	$Na_2O \cdot V_2O_4 \cdot 5V_2O_5$	—	
33 То же	$2Na_2O \cdot V_2O_4 \cdot 11V_2O_5$		

1) Compound
2) Formula
3) Melting point, °C
4) Possible reactions of compound, °C
5) Aluminum oxide
6) Aluminum sulfate
7) 700°C to Al_2O_3
8) Calcium oxide
9) Calcium sulfate
10) Ferric oxide
11) Ferric sulfate
12) Magnesium oxide
13) Magnesium sulfate
14) Nickel oxide
15) Nickel sulfate
16) Silicon dioxide
17) Sodium sulfate
18) Sodium disulfate
19) Sodium pyrosulfate
20) Vanadium trioxide
21) Vanadium tetroxide
22) Vanadium pentoxide
23) Zinc oxide
24) Zinc sulfate
25) Sodium metavanadate
26) Sodium pyrovanadate
27) Sodium orthovanadate
28) Nickel pyrovanadate
29) Nickel orthovanadate
30) Iron metavanadate
31) Iron vanadate
32) Sodium vanadylvanadate
33) Same.

TABLE 4.57

Composition of Fuel Ash and Deposits from Gas-Turbine Installations

1 Марка топлива и продолжительность испытаний на установке	2 Состав золы и отложений, мас. %						
	V_2O_5	Na_2O	SiO_2	Fe_2O_3	CaO	MgO	SO_3
3 Мазут 40 прямой перегонки:							
4 зола топлива	9,48	28,84	3,20	3,97	18,8	4,8	25,90
5 отложения с направляющих лопаток; 113 ч	12,56	19,71	1,34	3,58	3,69	0,75	27,62
6 отложения с рабочих лопаток	11,50	23,22	1,72	2,86	1,75	0,45	29,30
7 Мазут 60, образец 1:							
4 зола топлива	18,46	21,53	2,00	4,93	12,00	7,38	33,20
5 отложения с направляющих лопаток; 91 ч	16,84	29,05	0,75	1,35	1,96	1,99	—
6 отложения с рабочих лопаток	13,77	29,16	1,82	3,45	—	—	—
8 отложения с трубок регенератора	1,88	4,74	1,83	—	—	—	—
9 Мазут 60, образец 2:							
4 зола топлива	18,67	17,87	7,78	2,65	7,08	10 Следы	—
5 отложения с направляющих лопаток; 73 ч	10,02	29,16	0,65	1,00	3,24	—	31,90
6 отложения с рабочих лопаток	11,06	16,37	0,73	1,39	3,23	—	48,26
8 отложения с трубок регенератора	0,52	1,01	1,43	14,82	0,78	—	—
11 Мазут 40 с присадкой, образец 1:							
12 зола топлива 1	27 54	24,28	3,57	1,22	9,29	1,32	—
13 зола топлива 2	17,9	14,6	15,40	1,20	10,7	5,30	—
14 зола топлив (средний состав)	23,4	20,13	8,61	1,21	9,9	3,06	—
5 отложения с направляющих лопаток; 204 ч	17,46	22,36	11,88	1,44	1,18	1,63	—
15 Мазут 40 с присадкой, образец 2:							
12 зола топлива 1	13,1	14,50	18,00	1,50	4,9	2,40	18,8
13 зола топлива 2	29,6	13,80	16,80	1,30	11,3	2.80	17,9
16 зола топлива 3	29,3	16,80	17,70	1,20	10,3	2,80	43,0
14 зола топлив (средний состав)	22,24	15,13	17,65	1,36	7,14	2,63	26,7
5 отложения с направляющих лопаток	16,75	19,22	19,28	8,47	1,52	1,52	35,3
17 ДТ-2							
4 зола топлива	6,9	22,60	4,60	4,20	13,00	10,70	—
18 Мазут 40							
4 зола топлива	20,6	21,06	4,60	1,10	7,07	2,40	45,4

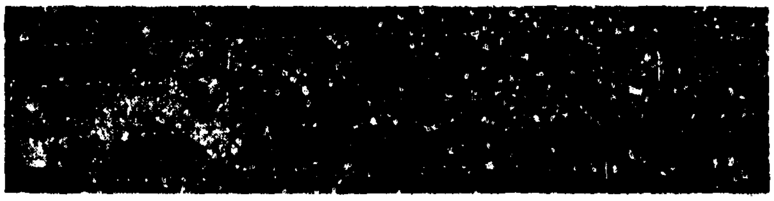
1) Fuel grade and test time on machine
2) Composition of ash and deposits, % by mass
3) Straight-run No. 40 mazout
4) Fuel ash
5) Deposits from guide vanes; ... h
6) Deposits from buckets
7) No. 60 mazout, specimen 1
8) Deposits from regenerator tubes
9) No. 60 mazout, specimen II
10) Traces
11) No. 40 mazout with additive, specimen 1
12) Fuel 1 ash
13) Fuel 2 ash
14) Ash from fuels (average composition)
15) No. 40 mazout with additive, specimen 2
16) Fuel 3 ash
17) DT-2
18) No. 40 mazout.

TABLE 4.58

Composition of Deposits Formed during Combustion of Sulfur-Containing and Low-Sulfur Mazouts

1 Мазуты	2 Место отбора проб	3 Содерж. нис. % влага	зола	SO_4	Cl	K	Na	Ca	Mg	Fe	Ni	Cr	Mn	V	SiO_2	6 нерастворимые окислы	7 органическая часть
8 Сернистый крекинг-мазут ($S = 1.9-2.5\%$)	9 Экранные трубы	1,5—5,6	8,0—37,3	6,4—41,9	10 Отсутствие	0—0,8	1,3—[illegible]	[illegible].3—10,2	10 Отсутствие	1,0—19,6	0—2,0	10 Отсутствие	11 Следы	0,1—1,3	0,1—2,3	0,1—0,7	14,3—86,0
	12 Конвективные трубы	0,8—4,5	68,4—96,8	23,5—60,6	13 То же	0—0,42	10,4—24,9	2,1—7,2	13 То же	1,2—3,6	1,4—4,5	13 То же	13 То же	0,6—1,0	0,2—3,0	0,01—16,2	2,1—76,5
	14 Пароперегреватель	2,9	84,2	57,4	13 »	10 Отсутствие	21,1	2,9	13 »	6,7	0,8	13 »	»	1,25	5,5	—	6,5
15 Сернистый мазут прямой перегонки ($S = 1.6-1.84\%$)	9 Экранные трубы	4,5	13,1	6,6	11 Следы	13 То же	2,4	0,9	10 Отсутствие	0,9	0,6	»	10 Отсутствие	0,1—0,5	4,6	2,7	80,5
	12 Конвективные трубы	1,7—3,6	59,1—86,5	42,0—48,5	0—0,14	0—0,9	12,1—19,2	0—1,9	0—0,4	0,4—10,9	0—0,8	»	0—0,7	0,1—0,4	6,6—14,9	5,2—10,8	6,7—94,5
	14 Пароперегреватель	4,2	66,9	21,7	11 Следы	10 Отсутствие	3,7	0,8	10 Отсутствие	12,3	3,5	»	11 Следы	0,1—0,4	—	10,7	20,7
16 Малосернистый мазут ($S = 0.3-0.66\%$)	9 Экранные трубы	0,7—4,5	17,3—31,0	8,2—36,0	10 Отсутствие	0—1,0	0,1—13,4	0,7—4,6	0—0,7	1,0—4,1	0,04—0,4	»	13 То же	10 Отсутствие	1,7—3,6	0,8—1,7	43,0—81,6
	12 Конвективные трубы	0,3—11,6	40,1—93,3	27,9—61,8	То же	0—1,6	6,9—25,8	1,4—5,8	0,4—1,4	1,0—11,3	0,3—3,9	»	»	То же	2,8—4,5	0,4—4,8	5,8—49,1
	14 Пароперегреватель	11,7	78,0	35,9	13 »	10 Отсутствие	1,8	3,8	10 Отсутствие	38,1	0,8	»	»	13 »	1,7	1,3	13,7

1) Mazout
2) Sample taken from
3) Content, %
4) Moisture
5) Ash
6) Insoluble oxides
7) Organic part
8) Sulfur-containing cracking mazout
9) Screen tubes
10) None
11) Traces
12) Convection tubes
13) Same
14) Steam preheater
15) Straight-run sulfur-containing mazout
16) Low-sulfur mazout.



1 2 3

Fig. 4.25. Appearance of 3Kh13 steel specimens after testing on laboratory model machine (gas temperature 650°C, time 5 h): 1) before testing; 2) exposed to combustion products of F12 mazout (V = 0%); 3) same, F5 mazout (V = 2.73%).

stickier and tougher. Gas turbines operated on Nos. 40 and 60 sulfur-containing mazouts fail after 1-2 days as a result of rapid deposit buildup.

At temperatures above 650°C, deposit formation is associated with the presence of vanadium [36]. It is assumed that when the mazout burns, the vanadium is converted to the trioxide V_2O_3 (a black oxide with weakly alkaline properties) and the tetroxide V_2O_4 (a blue-violet oxide with amphoteric properties), and that these are converted to V_2O_5 in an oxidizing medium at temperatures below 1200°C (the latter is a yellow oxide with distinct acidic properties). At temperatures of 600-700°C, vanadium pentoxide melts and is deposited on the heating surfaces of boilers and gas turbines. Owing to its adhesive properties, it traps and bonds the other ash elements of the fuel. Contact between vanadium oxide and sodium may result in the formation of the low-melting vanadates $NaVO_3$; $Na_4V_2O_7$; Na_3VO_4, and the complex vanadylvanadate compound $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$, which melts at 625°C. At temperatures below 600-650°C, the chief cause of deposit formation is found in the sulfates, and the sodium sulfates in particular. Vanadium and sodium deposits cause intensive corrosion of metallic surfaces of boilers and the in-stream parts of gas turbines.

High-temperature or "vanadium" corrosion results in accelerated oxidation of metal (Fig. 4.25) or intergranular failure. It appears at 650°C and above when the fuels contain $1 \cdot 10^{-3}$% of vanadium or more. With increasing fuel vanadium content, the temperature at which the corrosion appears decreases (Table 4.59).

Corrosion is intensified when vanadium and sodium are present together. The aggressiveness of vanadium is manifested most strongly when the fuel ash contains about 50% of it and at the proportions 87% V_2O_5 and 13% Na_2O_4 (Fig. 4.26) [35]. According to Ye.E. Evans, the corrosion of iron alloys becomes most intense at a 13:1 vanadium-to-sodium ratio (% by mass). Together with the corrosion increase, the static, fatigue, and long-term strength and plasticity of steels decrease simultaneously.

In steam boilers, vanadium corrosion is seldom observed at the prevailing steam parameters; the recorded cases pertain to

TABLE 4.59

Temperature of Appearance of Vanadium Corrosion as a Function of Vanadium Content in F5 Fleet Mazout

A Сталь	B Температура резкого возрастания коррозионных потерь (в °C) при содержании ванадия в топливе, $\% \cdot 10^{-3}$				
	0	1	2	3	3,5
C ЭИ-437Б	D Нет до 850	750	660	645	620
E ЭИ-435	F То же	750	660	645	620
G ЭИ-602	»	700	655	640	620

A) Steel
B) Temperature of sharp increase in corrosion losses (in °C) at fuel vanadium content of ..., $\% \cdot 10^{-3}$
C) EI-437B
D) None up to 850
E) EI-435
F) Same
G) EI-602.

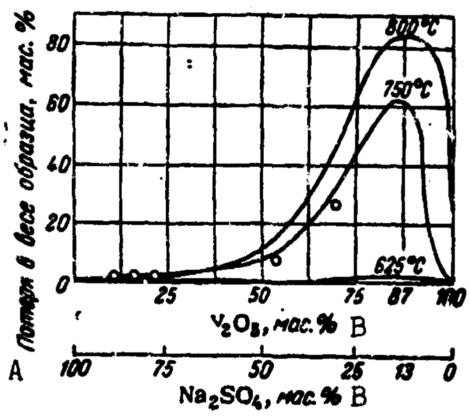


Fig. 4.26. Corrosion of EYaIT steel as a function of $V_2O_5:Na_2SO_4$ ratio (test time 60 h): o) corrosion of EYaIT steel at 750°C by natural deposits taken from buckets of GT-600-1.5 and boilers operated on sulfur-containing fuels. A) Specimen weight loss, % by mass; B) % by mass.

TABLE 4.60

Chemical Composition of High-Temperature Steels and Alloys

A Сталь	B Содержание химических элементов, %												
	C	Si	Mn	Cr	Ni	Ti	Nb	Mo	Fe	P	S	Al	C Другие элементы
D ЭЯ1Т	0,10	0,51	0,9	17,8	9,3	0,5	—	—	E Основа	—	—	—	—
F ЭИ-405	0,11	0,46	0,72	14,1	13,2	—	1,36	2,5	G Остальное	—	—	—	—
H Нимоник	0,06	0,48	0,40	18,7	G Остальное	1,56	1,4	—	—	—	—	—	—
ЭИ-417	0,11	0,76	1,24	24,10	18,47	—	—	—	G Остальное	0,022	0,013	—	—
ЭИ-481	0,34	0,62	8,67	12,56	7,82	0,07	0,36	1,35	I То же	0,023	0,013	—	1,43V
ЭИ-612	0,06	0,28	1,02	15,05	37,00	1,32	—	—	»	0,010	0,009	—	3,39W
J ЭИ-437Б	0,05	0,31	0,33	20,45	E Основа	2,45	—	—	0,33	0,006	0,007	0,80	0,03Cu; 0,01B; Ce : Pb = 0,1 : 0,005
ЭИ-607	0,02	0,37	0,72	15,55	G Остальное	1,92	—	—	0,92	0,010	0,006	1,65	—
ЭИ-765	0,08	0,21	0,23	14,38	E Основа	—	—	2,09	0,84	0,007	0,007	1,99	4,89W
ЭИ-725	0,05	0,63	0,55	14,74	34,77	—	—	—	41,10	0,005	0,009	—	4,64W
ЭИ-617	0,08	0,44	0,31	14,35	E Основа	2,10	—	3,76	1,44	0,012	0,005	2,10	5,69W 0,18V, 0,15Co, B — по расчету K

A) Steel
B) Content of chemical elements, %
C) Other elements
D) EYalT
E) Base
F) EI-...
G) Remainder
H) Nimonic
I) Same
J) EI-437B
K) By calculation.

high-temperature rapid corrosion of steam-regenerator tubing. The high corrosive aggressiveness of vanadium comes into evidence when boiler fuels are used for gas turbines (the working temperatures of the in-stream parts are 600-800°C and higher). In this case, the rate of vanadium corrosion will depend not only on the vanadium content in the mazouts and the operating temperature, but also on the chemical composition of the steels.

Nickel-base alloys are subject to considerably less vanadium corrosion than iron-base alloys (Fig. 4.27). The alloy nimonic (which has a nickel base) exhibits the greatest stability against vanadium corrosion. With molybdenum present in steels (steel EI-435), corrosion stability drops off sharply. Steel EI-481 also shows lower than normal stability, which is explained by its contents of molybdenum and vanadium and its high carbon content.

Because of their corrosion, the steels listed in Table 4.60 cannot be used in the production of gas turbines to operate on mazouts with high vanadium contents at gas temperatures of 700°C or higher.

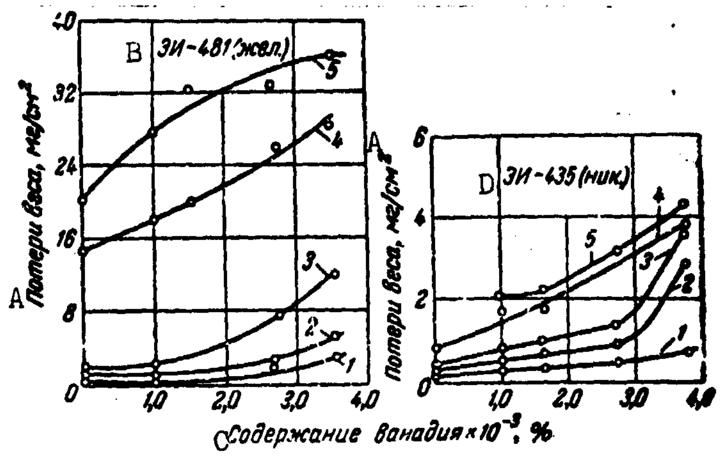


Fig. 4.27. Corrosion of nickel- and iron-base steels as a function of vanadium content. Gas temperatures (°C): 1) 600; 2) 630; 3) 680; 4) 800; 5) 850. A) Weight loss, mg/cm²; B) EI-481 (iron); C) vanadium content × 10^{-3}, %; D) EI-435 (nickel).

Vanadium corrosion is inhibited with the aid of special additives and by diffusion coating of steels. MgO, $MgSO_4$, clay, fuller's earth, kaolin, ammonia, and the magnesium salt of oxidized patrolatum, which is soluble in the fuel, are acknowledged to be the best additives. Magnesium additives are most effective in the proportions MgO:V = 4.5, $MgSO_4$:V = 9 or Mg:V = 3:1 [35, 37, 39, 40]. Among the diffusion coatings, those produced in siliconizing and chroming are most effective [38, 41].

The buildup of deposits on heating surfaces and their corrosion can also be reduced by lowering the ash content of the mazouts (by a factor of 2-4) by scrubbing the fuels with water and by separation using deemulsifiers [42]. This lowers ash content for the most part by lowering the sodium and calcium contents. The vanadium content is practically unaffected.

Sulfur Content in Liquid Boiler Fuel

The sulfur content of mazouts depends on the sulfur content in the crude petroleum (Table 4.61).

Sulfur may be present in the form of elementary sulfur, hydrogen sulfide, and various organic compounds (mercaptans, sulfides, disulfides, etc.). Much smaller amounts of the most aggressive and toxic compounds (hydrogen sulfide, elementary sulfur and mercaptans) are present in mazouts than in the crude petroleum or light runnings. The contents of sulfur compounds in mazouts are shown in Table 4.62.

When sulfur-containing fuels are burned, intensive corrosion of heating surfaces is observed at points where it is possible for the vapors present in the smoke gases to condense (downstream surfaces – air preheaters, water economizers, iron smokestacks). In this case, we have the so-called electrochemical (or sulfuric acid) corrosion.

TABLE 4.61

Sulfur Content in Petroleums and Products Obtained from Them

A Содержание серы, %			
B в нефти	C в бензине (до 200° С)	D в керосине (200—300° С)	E в мазуте
2,40	0,58	2,32	3,0
2,54	0,42	2,14	3,17
2,83	0,24	1,92	3,39
3,0	0,67	2,67	3,8

A) Sulfur content, %
B) In petroleum
C) In gasoline (below 200°C)
D) In kerosene
E) In mazout.

TABLE 4.62

Content of Active Sulfur Compounds in Mazouts [14]

1 Продукты	2 Всего серы, %	3 До нагревания, %				8 После нагревания в течение 5 ч до 90—95° С, %		
		4 сероводорода	5 элементарной серы	6 летучих соединений меркаптановой серы	7 меркаптановой серы	4 сероводорода	5 элементарной серы	6 летучих соединений меркаптановой серы
9 Сернистый мазут	3,04	0,0019	0,014	0,0075	0,0175	0,0021	0,018	0,012
	3,10	0,0021	0,0058	0,0087	0,0138	0,0025	0,009	0,013
	3,68	0,0022	0,017	0,021	0,0244	0,0028	0,018	0,022
10 Малосернистый мазут	0,54	0,0020	0,0008	0,007	Отсутствие 11	0,0020	0,002	0,008

1) Product
2) Total sulfur, %
3) Before heating, %
4) Hydrogen sulfide
5) Elementary sulfur
6) Volatile mercaptan sulfur compounds
7) Mercaptan sulfur
8) After heating for 5 h to 90-95°C, %
9) Sulfur-containing mazout
10) Low-sulfur mazout
11) None.

When sulfur-containing fuels are burned, the sulfur is converted to SO_2; however, SO_3 is also detected in combustion products. The conversion of SO_2 to SO_3 in combustion of mazouts represents from 3.2 to 7.4% for small fireboxes [43] and from 0.5 to 4.0% for large ones. According to the literature [44], from 5 to 9% of the sulfur present in the fuel is converted to SO_3. When sulfur-containing mazouts are burned, the SO_3 content in the smoke

gases (by volume) may reach 0.005%. SO_3 formation depends on the sulfur content in the fuel, the combustion (load) temperature, and the excess-air ratio. It has been reported that SO_3 formation depends on the catalytic action of sulfates and iron oxide, as well as that of vanadium. The dependence of SO_3 formation on fuel sulfur content and temperature is shown in Fig. 4.28. With rising flame temperature, the amount of SO_3 first increases and then approaches a constant value at a flame temperature above 1750°C; when the excess-air ratio is increased from 1.1 to 1.7, oxidation of SO_2 to SO_3 is doubled [43].

The presence of SO_3 in the smoke gases raises the effective initial water-condensation temperature to 120-150°C as against 45-65°C, which corresponds to the partial pressure of pure water vapor in the combustion products [44]. Figure 4.29 shows the smoke-gas dew point as a function of sulfur content [45], while Fig. 4.30 shows it as a function of sulfur content and the amount of air used in combustion.

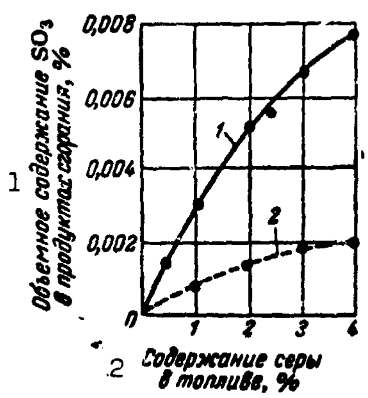


Fig. 4.28. SO_3 content in combustion products as a function of fuel sulfur content. Firebox wall temperatures: 1) 1200°C; 2) 1600°C. A) Content of SO_3 by volume in combustion products, %; B) sulfur content in fuel, %.

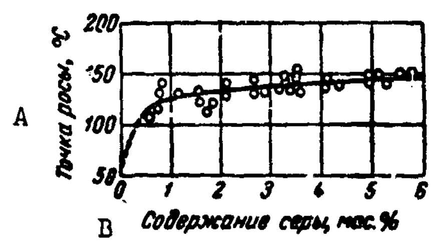


Fig. 4.29. Dew point as a function of sulfur content. A) Dew point, °C; B) sulfur content, % by mass.

Since the rear surfaces of boilers (air preheaters, economizers) have temperatures equal to or below the dew point of the smoke gases from sulfur-containing mazouts, it is on these surfaces that most of the sulfuric acid condenses. In the presence of deposits on the heating surfaces, the acid enters the deposits and remains there in the form of free sulfuric acid, which penetrates to the surface of the metal and intensifies its corrosion. Table 4.63 shows the free sulfuric acid contents in deposits. The rate of corrosion under exposure to sulfuric acid depends on the

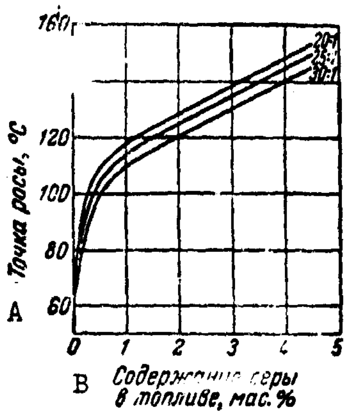


Fig. 4.30. Dew points measured in operation on fuels with various sulfur contents. The numerals on the lines indicate the air:fuel ratio. A) Dew point, °C; B) sulfur content in fuel, % by mass.

TABLE 4.63

Free Sulfuric Acid Content* in Deposits [2]

1 Место отбора проб отложений	2 Содержание свободной H_2SO_4, %	
	3 мазут ФС5 (S = 1,8%)	4 мазут Ф12 (S = 0,8%)
5 С нижних рядов труб экономайзера . . .	5,36	1,22
6 С верхних рядов труб экономайзера (у газохода)	0,81	7 отс
7 С труб конвективного пучка	отс	отс

*Acid determined by method of Yu.M. Kostrikin and V.N. Rumyantseva.

1) Deposit-sampling point
2) Free H_2SO_4 content, %
3) FS5 mazout
4) F12 mazout
5) From lower rows of economizer tubes
6) From upper rows of economizer tubes (at gas duct)
7) None
8) From convection-bundle tubes.

TABLE 4.64

Compositions of Steels

1 Материал	2 Содержание, %						
	C	Mn	Cr	Ni	Cu	Fe	Прочие 3
4 Инконель	0,08	0,25	14	78,7	—	6,5	—
5 Карпентер 20	0,07	0,75	20	29	3	44,2	2
6 Сталь 304	0,05	1,5	19	10	—	68	—
7 Сталь 310	0,2	1,5	25	20	—	52	—
8 Картен	0,1	0,4	0,9	0,45	0,4	97,0	—

1) Material
2) Content
3) Other
4) Inconel
5) Carpenter 20
6) Steel 304
7) Steel 310
8) Cor-ten.

acid's concentration, which, in turn, depends on wall temperature [46, 47].

According to VTI data, insignificant corrosion takes place when sulfur-containing mazouts are burned with a wall temperature of 65-105°C, while corrosion is intensive at temperatures from 110°C to the dew point of the sulfuric acid and below 65°C [47, 55].

Protection of the heating surfaces by raising the wall temperature also raises the temperature of the exhaust gases and lowers the efficiencies of boiler plants substantially. Use of corrosion-resistant steels for the rear heating surfaces involves great difficulty, since the corrosion rate of each metal may be either highest or lowest at a given acid concentration, and the concentration of the condensed acid is not constant because of the varying temperatures of the heating surfaces. According to [48], the high alloys inconel and carpenter 20 have low corrosion rates. Steels 304 and 310 are also recommended [49]. Among the less expensive low-alloy steels, cor-ten steel, which contains up to 97% iron and small additives of Mn, Cr, Ni, and Cu, has been suggested [45]. This steel has good resistance in the H_2SO_4 concentration range from 40 to 90%, i.e., under conditions similar to those actually encountered. The compositions of steels are shown in Table 4.64.

Little study has been given the influence of sulfur on the corrosive aggressiveness of fuels at high temperatures (from 600°C up). It has been established [50] that the rates of corrosion of most high-temperature alloys by the combustion products of distillate fuels containing up to 1% sulfur are even somewhat lower than when low-sulfur fuels are burned. Increasing the sulfur content in the fuel to 1.4-1.6% causes some intensification of corrosion. In residual fuels with vanadium, sulfur intensifies the vanadium corrosion of iron alloys, while not affecting the corrosion of nickel-base alloys [39].

REFERENCES

1. Losikov, B.V., Puchkov, N.G., Englin, B.A., Osnovy primeneniya nefteproduktov [Fundamentals of the Application of Petroleum Products], Gostoptekhizdat, 1959.

2. Fat'yanov, A.D., in collection "Motornyye topliva, masla i zhidkosti" [Motor Fuels, Oils and Additives], edited by K.K. Papok and Ye.G. Semenido, Gostoptekhizdat, 1957.

3. Geller, Z.I., Vysokovyazkiye mazuty kak kotel'noye i pechnoye toplivo [High-Viscosity Mazouts as Boiler and Furnace Fuels], Gostoptekhizdat, 1959.

4. Nefteprodukty i produkty pererabotki tverdykh topliv (Tekhnicheskiye trebovaniya) [Petroleum Products and Products from the Refining of Solid Fuels (Technical Specifications)] Standartgiz, 1963.

5. Kozhevnikov, A.V., Tyazheloye zhidkoye toplivo dlya

gazovykh turbin [Heavy Liquid Fuel for Gas Turbines], Gostoptekhizdat, 1958.

6. Karabin, A.I., Szhiganiye zhidkogo topliva v promyshlennykh ustanovkakh [Combustion of Liquid Fuel in Industrial Installations], Metallurgizdat, 1957.

7. Topliva i masla, primenyayemyye za rubezhom [Fuels and Oils Used Abroad], ITEIneftegas, 1963.

8. Perlov, G.V., Sudovyye parovyye kotly [Marine Steam Boilers], Sudpromgiz, 1961.

9. Teplovoy raschet kotel'nykh agregatov (normativnyy metod) [Thermal Calculation for Boiler Installations (Standard Method)] edited by A.M. Gurvich, N.V. Kuznetsov, Gosenergoizdat, 1957.

10. Berman, S.S., Forsunki i mazutnoye khozyaystvo goryachikh tsekhov [Nozzles and Boiler-Room Mazout Economy], Gostoptekhizdat, 1950.

11. Grigoryan, G.M., Dvoretskiy, A.I., et al., Primeneniye vyazkikh kreking-ostatkov v kachestve topochnogo mazuta [Use of Viscous Cracking Residues as Firebox Mazout], GONTI, 1939.

12. Rabinovich, G.G., Raschet nefteperegonnoy apparatury [Design of Petroleum-Distilling Apparatus], Gostoptekhizdat, 1941.

13. Emirdzhanov, R.T., Osnovy rascheta neftezavodskikh protsessov i apparatov [Fundamentals of the Design of Petroleum-Refinery Processes and Equipment], Aznefteizdat, 1956.

14. Dvoretskiy, A.I., Sernistyye mazuty kak energeticheskoye toplivo [Sulfur-Containing Mazouts as High-Energy Fuel], Gosenergoizdat, 1943.

15. Dvoretskiy, A.I., Elektricheskiye stantsii No. 9, 1957.

16. Papok, K.K., Ragozin, N.A., Tekhnicheskiy slovar' po toplivu i maslam [Technical Dictionary for Fuels and Oils], Gostoptekhizdat, 1963.

17. Vitman, L.A., Katsnel'son, B.D., Paleyev, P.I., Raspylivaniye zhidkosti forsunkami [Atomization of Liquids by Nozzles], Gosenergoizdat, 1962.

18. Chernozhukov, N.I., Guttsayt, N.M., Izv. VTI, 2, 36 (1930).

19. Kantorovich, B.V., Ivanov, V.M., et al., Khimiya i tekhnologiya topliv i masel, No. 1 (1957).

20. Nagiyev, M.F., Pererabotka neftyanykh ostatkov i ispol'-

zovaniye yeye produktov [Refining of Petroleum Residues and Utilization of its Products], Izd. AN SSSR, 1957.

21. Korobtsov, I.M., Ginzburg, S.A., Neft. khoz., No. 1 (1958).

22. Losikov, B.V., Fat'yanov, A.D., Golovistikov, I.V., in collection "Fiziko-khimicheskiye i ekspluatatsionnyye svoystva sernistykh i kotel'nykh topliv" [Physicochemical and Operational Properties of Sulfur-Containing and Boiler Fuels], GOSINTI, 1958.

23. Smirnov, Ye.K., Progressivnyy sposob sliva vysokovyazkikh nefteproduktov [A Progressing Draining Method for High-Viscosity Petroleum Products], Neft. khoz., No. 9 (1957).

24. Tuf, I.A., Ioff, U.M., Rzhavskiy, Ye.A., Neft. khoz., No. 12 (1959).

25. Rzhavskiy, Ye.A., Sukhodol'skiy, I.C., Opyt ekspluatatsii ustanovki po obezvozhivaniyu mazutov i mazutnykh zachistok [Experience in Operation of a Plant for Dewatering Mazouts and Mazout Rinsing], Gostoptekhizdat, 1958.

26. Lenwrence, A.S., Killner, W.J., J. Inst. Petrol., 34, No. 299 (1948); Killner, W.J., J. Inst. Petrol., 39, No. 349 (1953).

27. Nikolayeva, N.M., Levchenko, D.N., Khimiya i tekhnologiya topliv i masel, No. 9 (1964).

28. Yutkevich, R.M., Shcherbakov, L.V., Khimiya i tekhnologiya masel, No. 1 (1965).

29. Levchenko, D.N., Khimiya i tekhnologiya topliv i masel, No. 4 (1960).

30. Nikolayeva, V.G., Dukhnina, A.Ya., Komarov, K.I., Levinson, G.I., collection "Prisadki k maslam i toplivam" [Oil and Fuel Additives], Gostoptekhizdat, 1961.

31. Garner, F.H., J. Inst. Petrol., 39, No. 353 (1953).

32. Zul'tser, P., IV Mezhdunarodnyy neftyanoy kongress [IVth International Petroleum Congress], Vol. VII, Gostoptekhizdat, 1957.

33. Salikov, A.P., Teploenergetika, No. 6 (1952).

34. Fat'yanov, A.D., collection "Motornyye, reaktivnyye i raketnyye topliva," edited by K.K. Papok, Ye.G. Semenido, Gostoptekhizdat, 1962.

35. Lipshteyn, R.A., Avetisyan, A.S., et al., in collection "Bor'ba s korroziyey dvigateley vnutrennego sgoraniya i

gazoturbinnykh ustanovok" [Anticorrosion Measures for Internal-Combustion Engines and Gas-Turbine Installations], Mashgiz, 1962.

36. Clark, F.E., Vanadium Ash Problems in Oil Fired Boiler, J. Am. Soc. Naval Engrs, 65, 2 (1953).

37. Kovalev, Ye.A., in collection "Bor'ba s korroziyey dvigateley vnutrennego sgoraniya i gazoturbinnykh ustanovok," Mashgiz, 1962.

38. Vedenkin, S.G., Maksimov, A.I., Sorokin, A.V., loc. cit.

39. Fat'yanov, A.D., Mikulin, Yu.V., loc. cit.

40. Nikolayeva, V.G., Korobov, A.Ya., et al., loc. cit.

41. Gorbunov, Ye.A., Kovalev, A.G., Pastukhova, A.G., loc. cit.

42. Yutkevich, R.M., loc. cit.

43. Grumley, P.H., Fletcher, A.W., J. Inst. Fuel, No. 29, 187 (1956).

44. Kropp, L.I., Korroziya khvostovykh poverkhnostey kotel'nykh ustanovok (obzor) [Corrosion of Rear Surfaces of Boiler Installations (a Survey)], Gosenergoizdat, 1958.

45. Rendl, L.K., Wilsdon, R.D., J. Inst. Fuel, 29, No. 188 (1956).

46. Balezin, S.A., Krasovitskiy, T.I., ZhPKh, 24, No. 2 (1951).

47. Kuznetsov, N.V., Petrosyan, R.A., O zashchite khvostovykh poverkhnostey kotel'nykh agregatov ot korrozii s gazovoy storony [Protection of Rear Surfaces of Boiler Units from Corrosion on the Gas Side], 1956.

48. Barkley, J.F., Bur. Mines, Rept. Invest., No. 55, 4996 (1953).

49. Cort, R.L., Trans. ASME, 78, No. 1 (1956).

50. Losikov, B.V., Fat'yanov, A.D., Mikulin, Yu.V., Aleksandrova, L.A., Energomashinostroyeniye, No. 2 (1962).

51. Fuks, G.I., Vyazkost' i plastichnost' nefteproduktov [Viscosity and Plasticity of Petroleum Products], Gostoptekhizdat, 1951.

52. Smirnov, Ye.K., Sliv vysokovyazkikh gruzov iz zheleznodorozhnykh tsistern [Drainage of High-Viscosity Loads from Railroad Tank Cars], Transzheldorizdat, 1949.

53. Sturgis, B.M., Problems Associated with the Use of Heavy

Fuels, August 1959.

54. Fat'yanov, A.D., in collection "Fiziko-khimicheskiye i ekspluatatsionnyye svoystva sernistykh i kotel'nykh topliv" [Physicochemical and Operational Properties of Sulfur-Containing and Boiler Fuels], GOSINTI, 1958.

55. Petrosyan, R.A., Teploenergetika No. 2 (1958).

Manuscript Page No.	Transliterated Symbols
244	р = r = rabochiy = working, operating
244	л = l = letuchiy = volatile
244	с = s = sukhoy = dry
244	г = g = goryuchiy = combustible
244	н = n = nizshiy = low
244	в = v = vysshiy = high
245	б = b = bomba = bomb
248	раб.обв. = rab. obv. = rabochaya, obvodnennyy = = working (watered)
250	кал = kal = kaloriynyy = calorie
250	усл = usl = uslovnyy = conventional
251	сг = sg = sukhoy gaz = dry gas
251	вп = vp = vodyanaya para = water vapor
251	макс = maks = maksimal'nyy = maximum
251	влг = vlg = vlazhnyye gazy = moist gases
251	гор = gor = goreniye = combustion
253	мин = min = minimal'nyy = minimum
265	ж = zh = zhidkost' = liquid
265	в = v = voda = water

Chapter 5

ADDITIVES FOR FUELS

Additives are substances added to fuels in small quantities to improve their use characteristics or preserve their original properties. One or more additives may be added to a fuel; a given additive may improve several properties of the fuel (multifunctional additives). As a rule, additives are introduced in small quantities (fractions of a per cent); some additives are used in quantities of 1-2% and more.

Addition of additives is a convenient and economical way to improve the qualities of a fuel and sometimes the only way of obtaining a fuel with the required qualities.

Additives may be used in fuels of all types: aviation and automotive gasolines, jet, diesel and boiler fuels (including residual fuels), and rocket fuels, both hydrocarbon and chemical [1, 2].

Fuel additives must meet the following general requirements:

1) complete combustion without formation of deposits;

2) no detrimental influence on other properties of the fuel;

3) good solubility in the fuel or in its components and limited solubility in water;

4) stability in fuel solutions under storage and use conditions;

5) compatibility with other additives used in the same fuel.

1. CLASSIFICATION OF ADDITIVES

A classification of additives appears in Table 5.1. The first two groups of additives - those that improve the motor propertie of fuel and their chemical stability - are used most extensively.

The relative demand for the basic types of additives can be judged from the following data (tentative calculations for 1965 for the USA, thousands of tons) [3]:

TABLE 5.1

Classification of Motor-Fuel Additives

Groups and types of additives	Type of fuel in which additives are used
I. Additives that improve fuel motor properties	
1. Antiknock additives	Aviation gasolines Automotive gasolines
2. Predetonation eliminators ("deposit modifiers")	Leaded automotive gasolines
3. Additives that improve combustion of fuel in engines, including those that raise cetane numbers	Jet and diesel fuels
II. Additives that improve stability of fuels during storage, shipment and use in engines	
1. Antioxidants	All types of fuels
2. Metal deactivators that suppress catalytic effect of metals on oxidation of fuels	Same
3. Dispersing stabilizers, which prevent formation of insoluble residues in fuels	Jet, diesel and boiler fuels
III. Additives that reduce detrimental effect of fuels on apparatus and mechanisms	
1. Anticorrosion additives, including rust inhibitors	All types of fuels
2. Fuel-system deposit detergents	Automotive gasolines
3. Additives that reduce deposits and wear in cylinder-piston group of engine	Diesel and jet fuels
4. Vanadium-corrosion inhibitors for gas turbines	Residual fuels
IV. Additives that facilitate use of fuels at low temperatures	
1. Antiicing additives	Gasolines
2. Fuel crystallization temperature depressors	Diesel and jet fuels
3. Additives that prevent formation of ice crystals in fuels	Aviation fuels
V. Other additives	
1. Dyes	Gasolines
2. Additives that prevent accumulation of static electricity	Distillate fuels
3. Additives that prevent microorganism spoilage of fuels	Jet fuels

Antiknock additives..................	417.5
Deposit "modifiers"..................	1.23
Antioxidants.........................	3.713
Metal deactivators...................	0.725
Dispersing stabilizers (data for 1961)	3.451
Corrosion inhibitors.................	2.275

Antiknock additives form the bulk of the additives used because of the high concentrations in gasolines, and also because gasolines predominate in the total consumption of motor fuels. Additives that correct predetonation ("deposit modifiers") are intended for high-grade automotive gasolines, the production and consumption of which are relatively small-scale.

Additives that improve the motor properties of jet and diesel fuels are produced in much smaller quantities.

Among group II additives, the antioxidants are encountered most commonly; they have been in use for more than 30 years. The remaining additives of this group were developed later. Among the group III additives, which reduce the harmful effects of the fuel on apparatus and mechanisms, the anticorrosion additives are most important and most extensively used; chief among them are the rust inhibitors, which have the important function of protecting engine fuel apparatus and pumping and shipping facilities.

Among the additives of group IV, which facilitate use of fuels at low temperatures, the aviation-fuel additives that prevent formation of ice crystals are most important.

Additives that prevent accumulation of static electricity have come into use comparatively recently; their action is based on improvement of the conductivity of the fuels. Very recently, additives with bactericidal properties have made their appearance; their development was prompted by establishment of the detrimental effect of the vital-activity products of microorganisms present in hydrocarbon fuels [4].

2. ADDITIVES THAT IMPROVE MOTOR PROPERTIES OF FUELS

Antiknock Additives

Additives of this group include substances that improve the fuel-combustion process in the engine, prevent detonation (antiknock additives), facilitate spontaneous ignition of the fuels in diesel engines (raise cetane number), and others.

On addition of antiknock additives to a fuel, its stability against detonation rises. The relative effectiveness of antiknock components, supplements and additives is shown in Table 5.2. The first antiknock to come into extensive practical use was tetraethyllead.

TABLE 5.2

Relative Effectiveness of Antiknock Additives [5]

1 Соединение	2 Формула	3 Относительная эффективность по отношению к бензолу
4 **Компоненты**		
5 Бензол	C_6H_6	1,0
6 Толуол	$C_6H_5CH_3$	1,3
7 Ксилол	$C_6H_4(CH_3)_2$	1,2
8 Этиловый спирт	C_2H_5OH	2,0
9 **Добавки**		
10 Толуидин	$C_6H_4(CH_3)NH_2$	10,0
11 Анилин	$C_6H_5NH_2$	13,5
12 Ксилидин	$C_6H_3(CH_3)_2NH_2$	15,0
13 **Присадки**		
14 Тетракарбонил никеля	$Ni(CO)_4$	300,0
15 Пентакарбонил железа	$Fe(CO)_5$	500,0
16 Тетраэтилсвинец	$Pb(C_2H_5)_4$	600,0

1) Compound
2) Formula
3) Relative effectiveness with respect to benzene
4) Components
5) Benzene
6) Toluene
7) Xylene
8) Ethyl alcohol
9) Supplements
10) Toluidine
11) Aniline
12) Xylidine
13) Additives
14) Nickel tetracarbonyl
15) Iron pentacarbonyl
16) Tetraethyllead.

Tetraethyllead

Tetraethyllead [TEL] (ТЭС) is a colorless transparent liquid that is heavier than water. Its properties are listed in Table 5.3.

The first portions added to the fuel have the greatest effect; when more is added, the octane numbers of gasolines increase only insignificantly (Tables 5.4, 5.5 and Fig. 5.1).

The receptiveness of fuels to TEL depends substantially on their content of sulfur compounds. In themselves, the sulfur compounds have practically no influence on the antiknock properties of hydrocarbon mixtures, but the effectiveness of TEL in hydrocarbon mixtures containing sulfur is sharply lower. Sulfur-organic compounds lower the effectiveness of TEL to different degrees, depending on their structure (Fig. 5.2), but, on the average, at a sulfur concentration of 0.05%, about half of all of the TEL added is used unproductively in reactions with sulfur-containing organic compounds (Fig. 5.3). The fraction of the TEL expended in reactions with sulfur-organic compounds remains constant regardless of the total TEL concentration (Table 5.6).

TABLE 5.3

Physical Properties of Lead Antiknock Additives and Scavengers [5, 6]

1 Показатели	2 ТЭС	3 ТМС	4 Бромистый этил	5 Дибромэтан	6 Дибромпропан	7 α-Монохлорнафталин
8 Формула	$(C_2H_5)_4Pb$	$(CH_3)_4Pb$	C_2H_5Br	$C_2H_4Br_2$	$C_3H_6Br_2$	$C_{10}H_7Cl$
9 Молекулярный вес	323,45	267,35	108,98	187,88	201,91	162,61
10 Плотность при 20° С, г/см³ . .	1,652	1,995	1,431	2,180	1,933	1,194
11 Температура, °С:						
12 кипения . . .	200	110	38	132	142	259
13 плавления	−130	−28	−118	+10	−56	−20
14 Давление насыщенных паров по Рейду при 20° С, мм рт. ст.	0,3	26,5	399,0	8,7	5,8	1,0

1) Index
2) TEL
3) Tetramethyllead [TML] (TMC)
4) Ethyl bromide
5) Dibromoethane
6) Dibromopropane
7) α-monochloronaphthalene
8) Formula
9) Molecular weight
10) Density at 20°C, g/cm³
11) Temperatures, °C
12) Boiling point
13) Melting point
14) Reid saturation vapor pressure at 20°C, mm Hg.

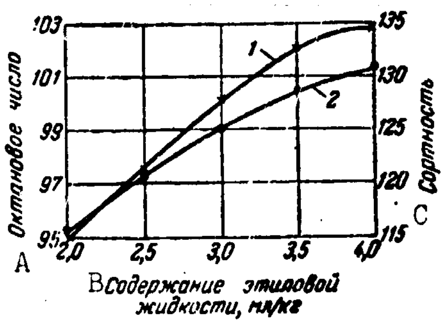


Fig. 5.1. Increase in octane and performance numbers (on rich mixture) on addition of R-9 ethyl fluid to B-100/130 aviation gasoline [7]: 1) performance number; 2) octane number. A) Octane number; B) content of ethyl fluid, ml/kg; C) performance number.

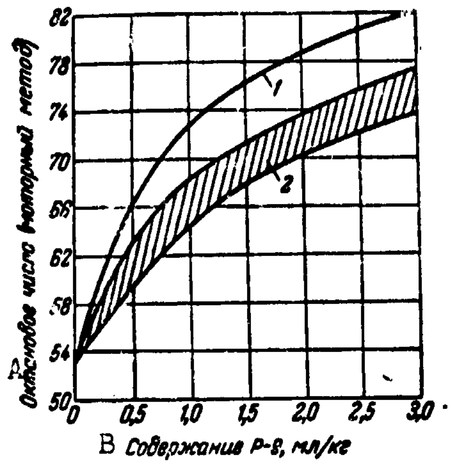


Fig. 5.2. Octane number (motor) of isooctane-heptane mixture as a function of tetraethyllead concentration [9]: 1) without sulfur; 2) in presence of 0.05% sulfur (experimental data on all sulfur-organic compounds fit into the shaded region). A) Motor octane number; B) R-9 content, ml/kg.

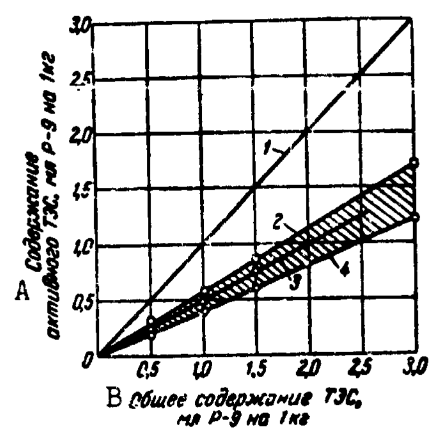


Fig. 5.3. Amount of "active" tetraethyllead as a function of total tetraethyllead concentration in fuel [9]: 1) without sulfur; 2) with isoamylmercaptan, 0.05% S; 3) average values for all sulfur-organic compounds (0.05% S); 4) with benzylmercaptan, 0.05% S. A) Active TEL content, ml of R-9 per 1 kg; B) total TEL content, ml of R-9 per 1 kg.

TABLE 5.4

Receptiveness of Certain Hydrocarbons and Gasolines to TEL [7, 8]

1 Топлива	2 Углеводороды, преобладающие в продуктах	3 Октановое число (моторный метод) при добавлении ТЭС, г/кг					
		0	0,82	1,64	2,46	3,28	4,10
4 н-Гептан	5 Нормальные парафиновые	0	30	44	55	60	—
6 Изооктан	7 Парафиновые изостроения	100	105	108	110	112	--
8 Алкилбензол	9 Ароматические	96	98	99	100	101	101
10 Алкилат	11 Парафиновые изостроения	91	97	101	103	105	106
12 Бензин Б-70 из бакинских нефтей	13 Нафтеновые	70	80	85	87	88	89
14 Бензин прямой перегонки из грозненских нефтей	15 Парафиновые	59	73	79	83	84	85
16 Бензин каталитического крекинга (двухступенчатого)	17 Парафиновые (52%) и ароматические (35%)	78	84	88	91	94	95

1) Fuel
2) Hydrocarbons predominating in the products
3) Octane number (motor) on addition of ... g/kg of TEL
4) *n*-heptane
5) Normal paraffinics
6) Isooctane
7) Isoparaffins
8) Alkyl benzene
9) Aromatics
10) Alkylate
11) Isoparaffinics
12) B-70 gasoline from Baku petroleums
13) Naphthenics
14) Straight-run gasoline from Groznyy petroleums
15) Paraffinics
16) Catalytic-cracking (two-stage) gasoline
17) Paraffinics (52%) and aromatics (35%).

TABLE 5.5

Receptiveness of Components of Automotive Gasolines to TEL [7]

A Бензин	B Групповой углеводородный состав, %				G Фракционный состав, °C					J Содержание серы, %	K Октановое число (моторный метод) при добавлении ТЭС, г/кг				L Прирост октанового числа при добавлении 0,41 г ТЭС на 1 кг
	C ароматические	D олефиновые	E нафтеновые	F парафиновые	H н. к.	10%	50%	90%	I к. к.		0,0	0,41	0,82	1,23	
M Прямой перегонки:															
N из туймазинской нефти	8	1	33	58	55	81	128	179	201	0,043	40	48	55	61	8
O из краснокамской нефти	5	1	30	64	53	80	118	161	181	0,07	48	56	61	65	8
P из среднеазиатской нефти	4	1	19	76	52	81	113	148	172	0,04	55	65	71	73	10
Q из ильской нефти	4	1	62	33	48	75	107	140	164	0,024	59	69	74	77	10
R из ходыженской нефти	3	1	39	57	40	62	93	114	164	0,004	64	75	79	82	11
S Термического крекинга:															
T парафинистой нефти	1	40	15	44	52	80	132	185	207	0,27	65	70	72	73	5
U нафтеновой нефти	3	33	31	33	46	81	139	186	204	0,08	71	75	79	80	4
V Каталитического крекинга:															
W тяжелого сырья	23	22	12	43	72	95	132	152	206	0,31	76	78	80	80	2
X легкого сырья	23	12	44	21	60	71	119	176	196	—	77	82	84	86	5
Y Каталитического риформинга (платформинга)	43	1	8	48	36	67	113	154	183	0,002	77	82	85	87	5

A) Gasoline
B) Group hydrocarbon composition, %
C) Aromatic
D) Olefinic
E) Naphthenic
F) Paraffinic
G) Fractional composition, °C
H) Start of boiling
I) End point
J) Sulfur content, %
K) Motor octane number on addition of ... g/kg of TEL
L) Increase in octane number on addition of 0.41 g of TEL per 1 kg

M) Straight-run
N) From Tuymazy petroleum
O) From Krasnokamsk petroleum
P) From Central Asian petroleum
Q) From Il'skiy petroleum
R) From Khodyzhensk petroleum
S) Thermal-cracking
T) Paraffin-base petroleum
U) Naphthene-base petroleum
V) Catalytic-cracking
W) Heavy crude
X) Light crude
Y) Catalytic reforming (platform process).

TABLE 5.6

Influence of Sulfur-Organic Compounds (0.05% S) on Tetraethyllead Receptiveness of a Mixture of 56% Isooctane + 44% Heptane [9]

1 Концентрация этиловой жидкости *, мл Р-9 на 1 кг	2 Октановое число ** без серы	3 Октилмеркаптан		5 Бензилмеркаптан		6 Пропилмеркаптан		7 Изоамилмеркаптан		8 Диэтилсульфид		9 Диизоамилсульфид		10 Дибутилдисульфид		11 Тиофан	
		4 октановое число	A ***	4 октановое число	A ***	4 октановое число	A ***	4 октановое число	A ***	4 октановое число	A ***	4 октановое число	A ***	4 октановое число	A ***	4 октановое число	A ***
0,5	66,0	60,0	42	59,1	36	61,0	50	62,4	60	61,8	56	61,6	53	59,7	40	63,0	65
1,0	72,8	65,4	44	64,7	41	67,1	53	67,3	55	67,2	54	66,5	50	65,0	42	67,5	57
1,5	76,1	68,5	42	67,9	38	70,9	56	70,8	55	70,8	55	69,8	50	67,9	39	70,6	55
3,0	82,0	73,4	37	74,3	40	76,1	48	77,4	53	77,0	52	76,0	48	73,8	38	—	—
		A сред.	41		39		51		55		54		50		40		59

*Here and below, the TEL concentration is given in ml of R-9 ethyl fluid (1 ml of R-9 ethyl fluid contains 0.82 g of TEL).

**Octane numbers determined by motor method.

***A is the percentage of active TEL - a quantity calculated by the formula

$$A = \frac{C}{C_0} \cdot 100$$

where C_0 is the practical TEL concentration; C is the TEL concentration found from the actual octane number according to the TEL receptiveness curve of the same fuel without sulfur compounds.

1) Concentration of ethyl fluid,* ml of R-9 per 1 kg
2) Octane number** without sulfur
3) Octylmercaptan
4) Octane number
5) Benzylmercaptan
6) Propylmercaptan
7) Isoamylmercaptan
8) Diethyl sulfide
9) Diisoamyl sulfide
10) Dibutyl disulfide
11) Thiophane.

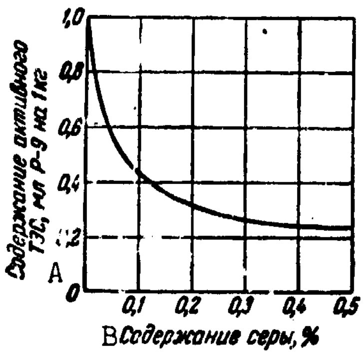


Fig. 5.4. Influence of sulfur concentration on amount of active TEL "A" [9] in mixture of hydrocarbons with benzylmercaptan (40% toluene, 30% heptane, 20% diisobutylene and 10% isooctane). A) Active TEL content, ml of R-9 per 1 kg; B) sulfur content, %.

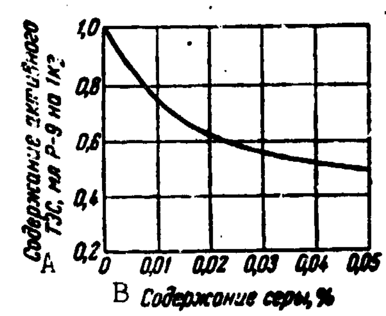


Fig. 5.5. Influence of sulfur concentration on amount of active TEL "A" [9] in mixture of hydrocarbons with diethyl sulfide (40% toluene, 30% heptane, 20% diisobutylene and 10% isooctane). A) Active TEL content, ml of R-9 per 1 kg; B) sulfur content, %.

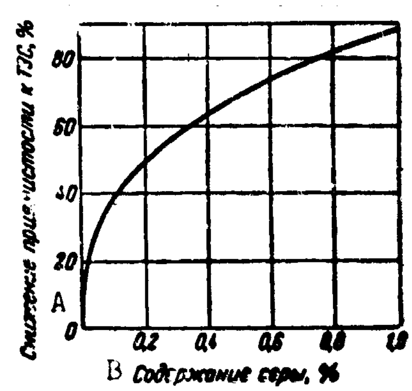


Fig 5.6. Decrease in TEL receptiveness as a function of sulfur concentration for an arbitrary gasoline with average sulfur-organic compound composition [9]. A) Loss of receptiveness to TEL, %; B) sulfur content, %.

The first portions of the sulfur compounds cause the greatest loss of TEL effectiveness (Figs. 5.4 and 5.5).

Figure 5.6 shows the decrease in TEL receptiveness as a func-

tion of sulfur concentration for a conventional fuel with average sulfur-compound composition (50% sulfides, 15% disulfides, 15% thiophenes and thiophanes, 10% mercaptans and 10% polysulfides). Sulfur-organic compounds also lower TEL detonation resistance during storage of fuels. The decrease in TEL effectiveness due to sulfur-organic compounds does not depend on the hydrocarbon composition of the fuels.

The receptiveness of gasolines to TEL is also lowered by certain halides (Table 5.7), phosphorus and other compounds [10, 11].

Tetraethyllead cannot be used in pure form as an antiknock additive for gasolines because the products of its combustion settle and accumulate on combustion-chamber walls in the form of scale and the engine stops running after a certain time. Halogen compounds - the so-called scavengers (Table 5.8) are used to remove the products of TEL combustion from the combustion chambers. Bromine-containing scavengers have come into widest use, since their effectiveness has been found to be higher than that of compounds containing chlorine (Fig. 5.7). Increasing the number of bromine atoms in the alkyl bromide molecule increases its effectiveness as a lead scavenger (Fig. 5.8).

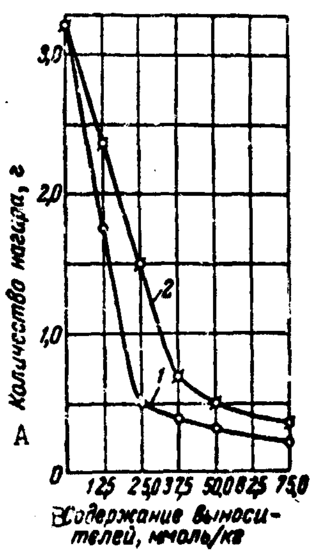


Fig. 5.7. Influence of scavenger concentration on buildup of deposits: 1) dibromomethanes; 2) dichloroethane. A) Amount of deposits, g; B) scavenger content, mmole/kg.

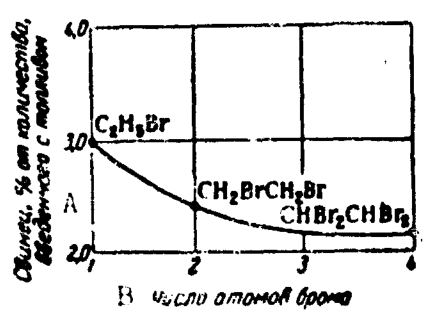


Fig. 5.8. Influence of degree of bromine substitution for hydrogen in scavenger molecule on deposition of lead in engine combustion chamber [12]. A) Lead, % of quantity introduced with fuel; B) number of bromine atoms.

TABLE 5.7

Influence of Organic Chlorides on Octane Number of Leaded Isooctane [13]

1 Добавляемые соединения хлора	2 Добавлено хлора, %	3 Октановое число (метод 1-С) с 3 мл этиловой жидкости на 1 кг топлива	4 Понижение октанового числа
5 Без добавления	—	113,5	—
6 н-Пропилхлорид	0,1	112,1	1,4
7 н-Бутилхлорид	0,1	112,7	0,8
8 трет-Бутилхлорид	0,1	105,4	8,1
9 н-Амилхлорид	0,1	112,0	1,5
10 трет-Амилхлорид	0,0009	113,6	0,0
11 То же	0,0092	112,9	0,6
»	0,0922	104,0	9.5

1) Chlorine compounds added
2) Chlorine added, %
3) Octane number (method 1-S) with 3 ml of ethyl fluid per 1 kg of fuel
4) Decrease in octane number
5) Without additive
6) *n*-propyl chloride
7) *n*-butyl chloride
8) *tert*-butyl chloride
9) *n*-amyl chloride
10) *tert*-amyl chloride
11) same.

TABLE 5.8

Influence of Scavengers on Deposit and Lead Buildup in Engine Combustion Chamber [12]

1 Состав антидетонатора	2 Количество нагара, снятого с каждой детали в камере сгорания, г/г, %				7 Общее количество нагара в камере сгорания, г	8 Содержание свинца в нагаре в камере сгорания, %	9 Количество свинца, введенного с бензином за время работы двигателя, г	10 Количество свинца, отложившегося в камере сгорания в виде нагара		12 Количество свинца, вынесенного из двигателя, %
	3 поршень	4 выпускной клапан	5 впускной клапан	6 головка цилиндра				11 г	%	
13 ТЭС без выносителя	0,41/6,5	3,21/50,7	0,05/0,8	2,66/42,0	6,33	84,35	52,8	5,34	10,10	89,90
14 ТЭС (1 моль) + бромистый этил (2 моль)	0,50/17,5	0,40/13,8	0,15/5,2	1,84/63,7	2,89	54,80	53,3	1,58	2,97	97,03
15 ТЭС (1 моль) + дибромэтан (1 моль)	0,34/13,3	0,36/14,1	0,45/17,6	1,40/55,0	2,55	55,58	50,1	1,41	2,81	97,19
16 То же	0,07/4,1	0,41/24,1	0,17/10,0	1,05/61,8	1,70	63,00	55,5	1,07	1,98	98,17

1) Composition of antiknock agent
2) Amount of deposits taken from each part in combustion chamber, g/g, %
3) Piston
4) Exhaust valve
5) Intake valve
6) Cylinder head
7) Total amount of deposits in combustion chamber, g
8) Lead content in combustion-chamber deposit, %
9) Quantity of lead introduced with gasoline during engine operation, g
10) Amount of lead deposited in combustion chamber as scale

11) g
12) Amount of lead removed from engine, %
13) TEL without scavenger
14) TEL (1 mole) + ethyl bromide (2 moles)
15) TEL (1 mole) + dibromoethane (1 mole)
16) Same.

Ethyl fluid is a mixture of TEL with a scavenger (see Table 5.9). TEL is poisonous, and adding it to gasoline increases their toxicity. To prevent accidents resulting from irregular use of leaded gasolines, it is mandatory that they be colored. For this purpose, dye is added to ethyl fluid. During storage, TEL is subject to oxidation and decomposition (Table 5.10); hence an antioxidant is introduced into the ethyl-fluid composition (see Table 5.9).

TABLE 5.9

Composition of Ethyl Fluids [8, 14]

1 Компоненты	2 Марка этиловой жидкости		
	3 Р-9	4 1-ТС	5 П-2
6 ТЭС, мас. %, не менее	54,0	58,0	55,0
7 Бромистый этил, мас. %, не менее	33,0	—	—
8 Дибромэтан, мас. %, не менее	—	33,0	—
9 Дибромпропан, мас. %, не менее	—	—	34,4
10 α-Монохлорнафталин, мас. %	6,8 ± 0,5	—	5,5
11 Красители, мас. %	0,1	0,5	0,1
12 Антиокислитель (*п*-оксидифениламин), мас. %	0,02—0,03	0,02—0,03	0,02—0,03
13 Наполнитель (керосин или бензин)	14 Остальное количество (до 100%)		

1) Component
2) Type of ethyl fluid
3) R-9
4) 1-TS
5) P-2
6) TEL, % by mass, no less than
7) Ethyl bromide, % by mass, no less than
8) Dibromoethane, % by mass, no less than
9) Dibromopropane, % by mass, no less than
10) α-monochloronaphthalene, % by mass
11) Dyes, % by mass
12) Antioxidant (*p*-hydroxydiphenylamine), % by mass
13) Thinner (kerosene or gasoline)
14) Remainder (to 100%).

TABLE 5.10

Oxidation Stability of Tetraethyllead [15]

1 Стабилизатор	2 Концентрация, г на 3 мл ТЭС	3 Число дней, необходимых для образования видимого осадка	4 Количество осадка, образовавшегося через 33 дня, мг на 33 мл ТЭС
5 Без стабилизатора	—	<3	156,5
6 N-*втор*-бутиламинофенол	0,06	<3	70,9
7 То же	0,1	<3	69,0
»	0,5	<3	40,3
8 Природный крезол	0,06	4	54,8
9 α-нафтол	0,025	7	81,6
10 Ди-*трет*-бутил-*п*-крезол	0,06	55	—
11 *н*-Дипропил-*п*-фенилендиамин	0,06	37	100,4
12 2,4-Диметил-6-*трет*-бутилфенол	0,06	>63	13 Нет
7 То же	0,1	68	»
»	0,5	66	»

1) Stabilizer
2) Concentration, g to 3 ml of TEL
3) Number of days necessary for formation of visible sediment
4) Amount of sediment formed after 33 days, mg to 33 ml of TEL
5) No stabilizer
6) N-*sec*-butylaminophenol
7) Same
8) Natural cresol
9) α-naphthol
10) Di-*tert*-butyl-*p*-cresol
11) *n*-dipropyl-*p*-phenylenediamine
12) 2,4-dimethyl-6-*tert*-butylphenol
13) None.

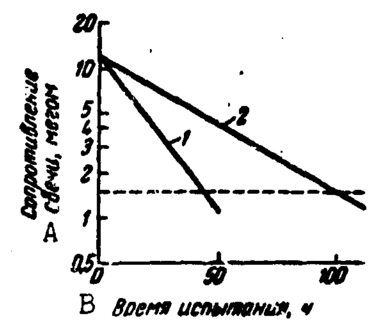


Fig. 5.9. Change in spark-plug resistance as a function of test time [22]: 1) leaded gasoline without additive; 2) leaded gasoline with tricresyl phosphate added (spark plug performs satisfactorily as long as its resistance remains above the value indicated by the broken line). A) Plug resistance, megohms; B) test time, h.

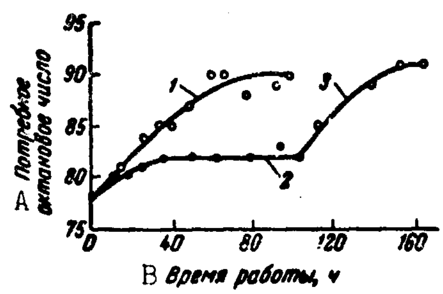


Fig. 5.10. Influence of additive containing boron on gasoline octane number required for automobile engine [29]: 1) without additive; 2) with butylboron additive; 3) experiment continued without additive. A) Required octane number; B) running time, h.

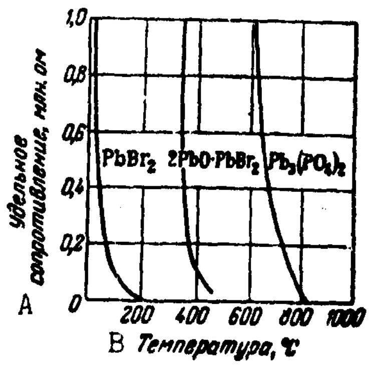


Fig. 5.11. Resistivity of deposits with various chemical compositions as a function of temperature [21]. A) Resistivity, megohms; B) temperature, °C.

TABLE 5.11

Fuel Octane Numbers [21] after Running Engine on Fuel Containing Phosphorus Additive (1100-2400 km Traveled)

A Номер автомобиля	B Необходимое октановое число бензина для уже работавшей машины	C Октановое число бензина для машины после работы на топливе с фосфорной присадкой	D Снижение требуемого октанового числа	A Номер автомобиля	B Необходимое октановое число бензина для уже работавшей машины	C Октановое число бензина для машины после работы на топливе с фосфорной присадкой	D Снижение требуемого октанового числа
1	90	88	2	5	94	86	8
2	90	86	4	6	96	88	8
3	92	86	6	7	96	96	0
4	94	90	4	8	94	92	2

A) Vehicle number
B) Required gasoline octane number for previously used engine
C) Gasoline octane number for engine after operation on fuel with phosphorus additive
D) Lowering of octane requirement.

TABLE 5.12

Influence of Lead Compounds on Spontaneous Ignition Temperature of Deposits [21]

Состав отложений 1	Углерод (сажа) 2	Углерод + свинцово-бромистые соединения 3	Углерод + свинцово-фосфорные соединения 4
5 Температура воспламенения отложений, °C	500	200—230	350—470

1) Composition of deposits
2) Carbon (soot)
3) Carbon + lead-bromine compounds
4) Carbon + lead-phosphorus compounds
5) Spontaneous ignition temperature of deposits, °C.

Even in the presence of scavengers, use of TEL as a gasoline antiknock additive results in heavy deposit formation (see Table 5.8), especially in modern automotive engines with high compression ratios (9 to 12). As a result of formation of the lead deposit in the combustion chamber, incandescent particles appear and may cause detonation of the mixture. Such uncontrolled ignition causes power losses, rough running, noise and an increase in the rate of engine wear [14, 16-21]. Lead scale on spark-plug electrodes may short-circuit them [21-23].

The performance of high-compression engines using leaded gasolines is improved by the use of additives that contain phosphorus or boron (Figs. 5.9-5.11 and Table 5.11).

The smaller number of cases of uncontrolled ignition in the presence of phosphorus additives is explained by the fact that lead-phosphorus complexes lower the ignition temperature of carbon to a lesser degree than do lead-bromine compounds (Table 5.12).

Tetramethyllead

Use of TEL in engines with moderate compression ratios and in gasolines with moderate octane ratings and moderate aromatic contents is more effective than the use of TML (Table 5.13). In high-

TABLE 5.13

Antiknock Effectiveness of Alkyllead Compounds when Added to Automotive Gasolines (According to F.B. Ashbel', A.L. Gol'dshteyn and K.N. Fastova)

A Алкилсвинцовое соединение	B Октановое число с добавками соединений, моль/кг		
	0,0	0,0025	0,0050
C Бензин, образец 1			
D Тетраметилсвинец	57,2	62,0	64,6
E Тетраэтилсвинец	57,2	64,6	70,2
F Тетраизопропилсвинец	57,2	63,4	66,6
G Бензин, образец 2			
D Тетраметилсвинец	55,8	62,5	65,0
H Этилтриметилсвинец	55,8	63,0	67,0
I Диэтилдиметилсвинец	55,8	63,0	67,5
J Триэтилметилсвинец	55,8	65,0	68,0
E Тетраэтилсвинец	55,8	64,3	68,2

A) Alkyllead compound
B) Octane number with ... mole/kg of compound added
C) Gasoline, specimen 1
D) Tetramethyllead
E) Tetraethyllead
F) Tetraisopropyllead
G) Gasoline, specimen 2
H) Ethyltrimethyllead
I) Diethyldimethyllead
J) Triethylmethyllead.

TABLE 5.14

Influence of Quantity of Aromatic Hydrocarbons in Gasolines on Relative Effectiveness of Tetramethyllead [TML] (TMC) [25]

A Содержание ароматических углеводородов в бензинах, %	B Октановое число с 0,8 мл/л ТЭС		E Улучшение антидетонационных свойств (разница между октановыми числом бензинов с ТМС и ТЭС)		
	C исслед. метод	D моторный метод	C исслед. метод	D моторный метод	F дорожный метод
48,1	104,7	96,3	0,3	1,4	2,1
43,0	100,5	88,2	0,3	0,8	1,0
39,0	100,3	90,5	0,5	0,6	1,6
33,0	99,4	88,1	0,1	0,7	0,9
32,0	99,3	87,8	−0,1	0,7	0,8
28,0	98,8	86,6	0,5	0,5	0,5
16,0	99,2	87,4	−1,6	0,1	0,6

A) Content of aromatic hydrocarbons in gasolines, %
B) Octane number with 0.8 ml/liter of TEL
C) Research method
D) Motor method
E) Improvement of antiknock properties (difference between octane numbers of gasolines with TML and TEL)
F) Road method.

TABLE 5.15

Comparative Antiknock Effectiveness of TEL and TML in Reforming Gasoline Containing 40% Aromatic Hydrocarbons [26]

1 Метод оценки антидетонационной стойкости	2 Октановое число бензина при добавлении	
	3 ТЭС	4 ТМС
5 Исследовательский	100,7	101,7
6 Моторный	92,6	93,5
7 Дорожный:		
8 на автомобиле с автоматической трансмиссией	99,8	101,0
9 на автомобиле с ручной трансмиссией	98,0	102,4

1) Method of determining antiknock stability
2) Octane number of gasoline on addition of
3) TEL
4) TML
5) Research
6) Motor
7) Road
8) Vehicle with automatic transmission
9) Vehicle with manual transmission.

TABLE 5.16

Effectiveness of TML and TEL in Mixtures* Containing Aromatic Hydrocarbons with Various Structures [27]

1 Ароматический компонент	2 Разница в значениях октановых чисел смесей, содержащих ТМС и ТЭС в количестве			
	3 0,28 г Pb на 1 мл		0,85 г Pb на 1 мл	
	4 исслед. метод	5 моторный метод	4 исслед. метод	5 моторный метод
6 Бензол	−2,2	−0,6	−1,3	−0,6
7 Толуол	−1,0	0,2	0,1	0,7
8 Этилбензол	−1,6	−2,0	−0,1	−0,7
9 *о*-Ксилол	−0,8	0,0	1,0	1,9
10 *м*-Ксилол	−0,2	0,9	0,4	1,5
11 Изопропилбензол	−2,0	−2,0	−1,0	−1,3
12 1, 2, 4-Триметилбензол	−0,9	0,5	0,7	2,8
13 *н*-Бутилбензол	−4,0	−3,0	−3,2	−2,2
14 *втор*-Бутилбензол	−1,6	−0,8	−0,5	0,0
15 *трет*-Бутилбензол	−2,0	−0,9	−0,8	−2,3

*Mixture of 40% 40-octane gasoline and 60% aromatic hydrocarbons.

1) Aromatic component
2) Difference between octane-number values of mixtures containing TML and TEL in amounts of
3) 0.28 g of Pb to 1 ml
4) Research method
5) Motor method
6) Benzene
7) Toluene
8) Ethylbenzene
9) *o*-xylene
10) *m*-xylene
11) Isopropylbenzene
12) 1,2,4-trimethylbenzene
13) *n*-butylbenzene
14) *sec*-butylbenzene
15) *tert*-butylbenzene.

octane gasolines, tetramethyllead has better antiknock stability than TEL [25]. When TEL is replaced by an equivalent amount of TML (with respect to the metal), the road octane numbers of the gasolines increase on the average by one or two units [25-31]. The maximum effect from the use of TML is observed when antiknock stability is rated under road conditions, and a smaller one when the octane ratings are determined by the motor method; substitution of TML for TEL has only an insignificant effect on research octane numbers (Tables 5.14, 5.15). An increase in the aromatics content in the gasoline raises the relative effectiveness of TML (see Table 5.14). In gasolines containing more than 30% of aromatic hydrocarbons, it is more advantageous to use TML than TEL [26]. The relative effectiveness of TML depends not only on the amount of aromatic hydrocarbons, but also on their structure (Table 5.16). With rising lead concentration [32] in the gasoline, the relative effectiveness of TML increases (Fig. 5.12).

The lower boiling point of TML by comparison with TEL and its higher saturation vapor pressure (see Table 5.3) favor the opera-

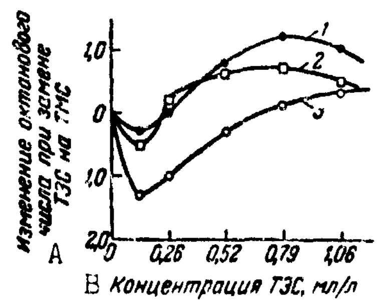


Fig. 5.12. Influence of lead concentration in gasoline on effectiveness of TEL and TML [32]. Octane numbers: 1) road; 2) motor; 3) research. A) Change in octane number on substitution of TML for TEL; B) TEL concentration, ml/liter.

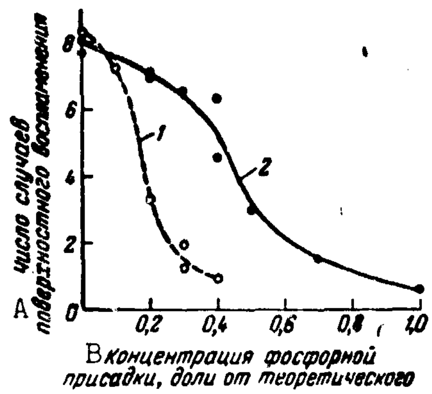


Fig. 5.13. Influence of concentration of phosphorus additive on number of cases of surface ignition in combustion of catalytic-reforming gasoline (66% aromatic hydrocarbons) with TEL and TML [33]: 1) gasoline with TML (0.84 g of lead per 1 liter); 2) gasoline with TEL (0.84 g of lead per 1 liter). A) Number of cases of surface ignition; B) concentration of phosphorus additive, fractions of theoretical.

TABLE 5.17

Properties of Tetraalkyl Derivatives of Lead and Their Mixtures [28]

A Соединения свинца	B Содержание свинца, вес. %	C Относительное давление насыщенных паров при 20° С	A Соединения свинца	B Содержание свинца, вес. %	C Относительное давление насыщенных паров при 20° С
D ТЭС	64,06	1	МЭС-500	70,15	17
E 75% ТЭС+25% ТМС	66,97	26	25% ТЭС+75% ТМС	73,64	75
F МЭС-250	66,97	5	МЭС-750	73,64	45
50% ТЭС+50% ТМС	70,15	51	ТМС	77,51	100

A) Lead compounds
B) Lead content, % by mass
C) Relative saturation vapor pressure at 20°C
D) TEL
E) 75% TEL + 25% TML
F) MEL-250.

TABLE 5.18

Effectiveness of Tetraalkyllead in Determination of Road Octane Ratings for Premium Gasoline [28]

A Показатели	B Тетраалкилы свинца						
	C МЭС-250	МЭС-500	МЭС-750	D 75% ТЭС 25% ТМС	50% ТЭС 50% ТМС	25% ТЭС 75% ТМС	ТМС
E Число автомобилей	3	8	3	1	8	4	5
F Количество оценок	43	184	48	15	173	86	85
G Среднее повышение эффективности по сравнению с ТЭС, дорожные октановые числа	0,02	0,39	0,16	0,24	0,54	0,80	0,42
H Количество случаев (в %), когда октановое число повышалось:							
I на 0,1 ед. и более	47	83	66	66	82	84	75
J на 0,5 ед. и более . . .	14	50	29	26	62	77	50

A) Index
B) Tetraalkyllead
C) MEL-250
D) 70% TEL, 25% TML
E) Number of vehicles
F) Number of evaluations
G) Average increase in effectiveness over TEL, road octane numbers
H) Number of cases (in %) in which octane number increased
I) By 0.1 unit or more
J) By 0.5 unit or more.

TABLE 5.19

Influence of Sulfur-Containing Compounds on Receptiveness of Gasolines to TML and TEL* [27]

1 Содержание серы	2 Понижение октанового числа по сравнению с бензином, не содержащим серы				1 Содержание серы	2 Понижение октанового числа по сравнению с бензином, не содержащим серы			
	3 исслед. метод		моторный метод			3 исслед. метод		моторный метод	
	5 ТМС	6 ТЭС	5 ТМС	6 ТЭС		5 ТМС	6 ТЭС	5 ТМС	6 ТЭС
7 Дисульфиды:					9 Тиофен:				
8 0,1% серы	4,0	2,2	4,7	3,8	8 0,1% серы	0,3	0,3	0,5	0,9
0,2% »	5,3	3,0	[illegible]	5,0	0,25% »	1,0	0,7	1,5	1,5

*0.85 g of lead to 1 liter of gasoline.

1) Sulfur content
2) Octane rating decrease by comparison with gasoline not containing sulfur
3) Research
4) Motor
5) TML
6) TEL
7) Disulfides
8) 0.1% sulfur
9) Thiophene.

tion of engines in which there is substantial nonuniformity of the distribution of the gasoline fractions among the engine's cylinders. For this reason, mixtures of TEL and TML and compounds such as triethylmethyllead (MEL-250), diethyl[di]methyllead (MEL-500) and ethyltrimethyllead (MEL-750) are prepared. The saturation vapor pressures of all these compounds and mixtures are higher than that of TEL (Table 5.17). Mechanical mixtures of TEL and TML are more volatile than the corresponding tetraalkyls with unlike radicals. TEL-TML mixtures with TML predominating are most effective (Table 5.18). TML is more sensitive to sulfur-organic compounds present in the gasolines than is TEL (Table 5.19).

When an engine is operated on a gasoline with TML, phosphorus additives suppress uncontrolled ignition by deposits more readily than in operation on a TEL gasoline (Fig. 5.13).

As regards their influence on other operational properties of gasolines, TML is practically equivalent to TEL. At the present time, the cost of TML is somewhat higher than that of TEL [25].

Additives that Enhance the Effect of Lead Antiknock Compounds

Organic acids, esters and various acid derivatives have been tested as additives to improve the effectiveness of lead antiknocks (Table 5.20).

TABLE 5.20

Effectiveness [34] of Various Compounds as TEL Promoters (0.8 ml of TEL to 1 liter of Fuel)

1 Соединение	2 Концентрация, моль/м	3 Изменение октанового числа	1 Соединение	2 Концентрация, моль/м	3 Изменение октанового числа
4 Карбоновые кислоты			13 β, β-Диметилакриловая	80	1,2
5 Уксусная	50	2,0	Бензойная 14	50	2,1
»	67	2,2	о-Толуиловая 15	40	1,6
»	83	2,5	п-Толуиловая 16	40	1,0
»	125	1,6	Фенилуксусная 17	43	0,9
6 Пропионовая	50	2,3	Метоксиуксусная 18	57	0,7
7 Масляная	44	2,3	Ацетилмолочная 19	95	1,7
8 Олеиновая	80	1,4	Муравьиная 20	43	0,2
9 Триметилуксусная	50	1,7	α-Оксидекановая 21	80	0,0
10 Циклогексанкарбоновая	80	2,2	Пировиноградная 22	80	−0,6
11 Акриловая	80	2,6	Салициловая 23	24	−1,6
12 Кротоновая	46	2,0	Нитроуксусная 24	48	−0,1

TABLE ..20 (continued)

25 Хлоруксусная	42	—3,3
26 β-Хлорпропионовая	80	—0,9
27 Диолеиновая	80	—1,0
28 Сложные эфиры		
29 Ацетилгликоль	44	1,4
30 *трет*-Бутилацетат	60	0,9
31 То же	86	1,1
»	103	1,2
32 *трет*-Бутилпропионат	77	0,9
33 *трет*-Бутилтриметилацетат	63	1,0
34 *трет*-Бутилметакрилат	84	1,2
35 *трет*-Бутилбензоат	56	1,4
36 *трет*-Бутил-*о*-метоксибензоат	106	1,0
37 *трет*-Бутил-*п*-нитробензоат	80	0,6
38 *трет*-Бутиловый эфир фуранкарбоновой кислоты	95	1,3
39 *трет*-Бутилметоксиацетат	80	0,6
40 *трет*-Бутилфеноксиацетат	80	0,7
41 *трет*-Бутиловый эфир ацетилгликолевой кислоты	55	1,1
42 Ди-*трет*-бутиловый эфир малоновой кислоты	80	0,5
43 *трет*-Бутиловый эфир муравьиной кислоты	40	—0,1
31 То же	80	0,0
»	120	0,1
44 Ди-*трет*-Бутиловый эфир щавелевой кислоты	40	—0,3
45 Ди-*трет*-бутиловый эфир янтарной кислоты	40	—0,1
46 Ди-*трет*-бутиловый эфир адипиновой кислоты	40	—0,5
47 Ди-*трет*-бутиловый эфир азелаиновой кислоты	30	—2,0
48 *трет*-Бутилцианацетат	106	—0,9
трет-Бутилнитроацетат 49	50	—3,2
трет-Бутил-*о*-хлорбензоат 50	80	—1,1
трет-Амилацетат 51	80	0,9
Терпенилацетат 52	83	1,2
1,1-Диметилпропенилацетат 53	80	1,3
α, α-Диметилфенилэтилацетат 54	61	1,1
Пропенилидендиацетат 55	75	0,7
Пинаколдиацетат 56	25	0,4
Метилацетат 57	81	—0,6
Изопропилацетат 58	49	0,2
Изобутилацетат 59	43	0,1
втор-Бутилацетат 60	69	0,1
Винилацетат 61	80	0,2
Изопропенилацетат 62	80	0,0
Фенилацетат 63	37	—0,1
Бензилбензоат 64	65	—0,2
Фурфурилацетат 65	43	—0,1
66 Производные карбоновых кислот и др.		
Уксусный ангидрид 67	80	1,9
Масляный ангидрид 68	80	1,6
69 Смесь муравьиного и уксуснокислого ангидридов 70	85	2,4
Смесь ангидридов муравьиной и уксусной кислот	110	2,3
Анилинпропионат 71	60	2,5
N-метиланилинацетат 72	90	3,3
N, N-диметиланилинацетат 73	40	1,8
Пиридинацетат 74	80	2,6
Бензойный ангидрид 75	50	0,0
Бензальдегид 76	94	0,0
Масляный альдегид 77	56	—0,1
Пропионовой альдегид 78	93	0,0

1) Compound
2) Concentration, mole/kg
3) Change in octane number
4) Carboxylic acids
5) Acetic
6) Propionic
7) Butyric
8) Oleic
9) Trimethylacetic
10) Cyclohexanecarboxylic
11) Acrylic
12) Crotonic
13) β,β-dimethylacrylic
14) Benzoic
15) *o*-toluic
16) *p*-toluic
17) Phenylacetic
18) Methoxyacetic
19) Acetyllactic
20) Formic
21) α-hydroxydecanoic
22) Pyruvic
23) Salicylic
24) Nitroacetic
25) Chloroacetic
26) β-chloropropionic
27) Dioleic
28) Esters
29) Acetyl glycol
30) *tert*-butyl acetate

31) Same
32) *tert*-butyl propionate
33) *tert*-butyltrimethyl acetate
34) *tert*-butyl methacrylate
35) *tert*-butyl benzoate
36) *tert*-butyl-*o*-methoxybenzoate
37) *tert*-butyl-*p*-nitrobenzoate
38) *tert*-butyl ester of furancarboxylic acid
39) *tert*-butyl methoxyacetate
40) *tert*-butyl phenoxyacetate
41) *tert*-butyl ester of acetylglycolic acid
42) Di-*tert*-butyl ester of malonic acid
43) *tert*-butyl ester of formic acid
44) Di-*tert*-butyl ester of oxalic acid
45) Di-*tert*-butyl ester of succinic acid
46) Di-*tert*-butyl ester of adipic acid
47) Di-*tert*-butyl ester of azelaic acid
48) *tert*-butyl cyanoacetate
49) *tert*-butyl nitroacetate
50) *tert*-butyl-*o*-chlorobenzoate
51) *tert*-amyl acetate
52) Terpenyl acetate
53) 1,1-dimethylpropenyl acetate
54) α,α-dimethylphenylethyl acetate
55) Propenylidene diacetate
56) Pinacol diacetate
57) Methyl acetate
58) Isopropyl acetate
59) Isobutyl acetate
60) *sec*-butyl acetate
61) Vinyl acetate
62) Isopropenyl acetate
63) Phenyl acetate
64) Benzyl benzoate
65) Furfuryl acetate
66) Carboxylic acid derivatives, etc.
67) Acetic anhydride
68) Butyric anhydride
69) Mixture of formic and acetic anhydrides
70) Mixed anhydrides of formic and acetic acids
71) Aniline propionate
72) N-methylaniline acetate
73) N,N-dimethylaniline acetate
74) Pyridine acetate
75) Benzoic anhydride
76) Benzaldehyde
77) Butyraldehyde
78) Propionaldehyde.

Addition of acids increases antiknock stability only in leaded gasolines. In the absence of TEL, the acids have no influence on gasoline octane ratings (Fig. 5.14). With increasing TEL content in the gasolines, the effectiveness of the added acid and its optimum concentration increase (Fig. 5.15). A considerable gain is achieved by adding acids to gasolines with higher octane ratings (Fig. 5.16). An increase in the aromatic-hydrocarbon content in the gasoline also increases the effectiveness of the acid additive (Fig. 5.17).

Addition of monocarboxylic acids is detrimental to some operational properties of gasoline (corrosive aggressiveness, washout of additives by water, etc.); in practice, therefore, only their derivatives can be used, especially *tert*-butyl acetate, which forms acetic acid and isobutylene on thermal decomposition. Compounds that manifest their activity only after decomposition are less effective than the original acids (Fig. 5.18). However,

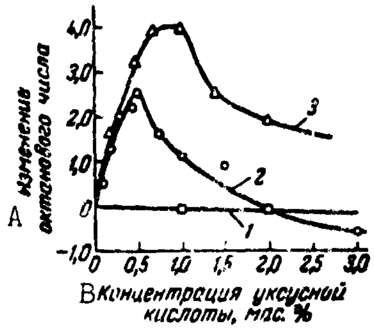


Fig. 5.14. Influence of acetic acid concentration on octane rating of gasoline (43% ar⌐m⌐tics, 16% olefinics, 41% paraffinic and naphthenic hydrocarb⌐ ; - octane rating 99.5) by research method [34]: 1) without TE..; 2) 0.8 ml of TEL to 1 liter; 3) 1.6 ml of TEL to 1 liter. A) Octane rating change; B) acetic acid concentration, % by mass.

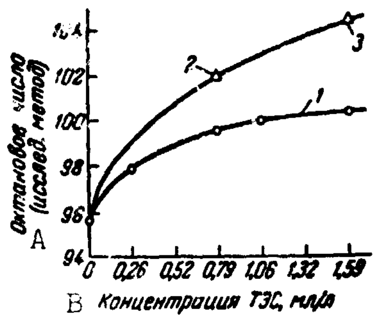


Fig. 5.15. Gasoline octane rating (see Fig. 5.14) as a function of TEL and acetic acid concentrations [34]: 1) without acetic acid; 2) 0.5% acetic acid; 3) 1.0% acetic acid. A) Research octane number; B) TEL concentration, ml/liter.

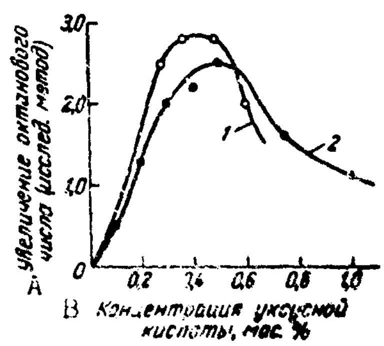


Fig. 5.16. Influence of initial octane number on receptiveness of gasolines to acetic acid [34]: 1) 104-octane gasoline; 2) 100-octane gasoline. A) Octane number increase (research method); B) acetic acid concentration, % by mass.

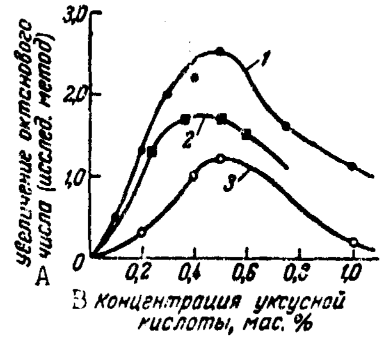


Fig. 5.17. Influence of amount of aromatic hydrocarbons on receptiveness of gasolines (original octane number 100) to acetic acid [34]: aromatic hydrocarbons: 1) 43%; 2) 36%; 3) 29%. A) Octane number increase (research method); B) acetic acid concentration, % by mass.

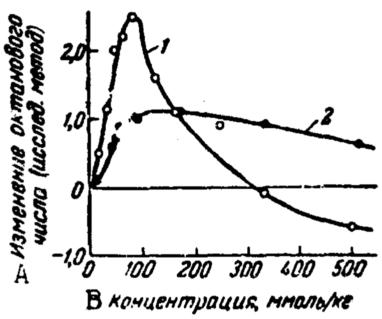


Fig. 5.18. Effectiveness of acetic acid and *tert*-butyl acetate [34]: 1) acetic acid; 2) *tert*-butyl acetate. A) Change in octane number (research method); B) concentration, mmole/kg.

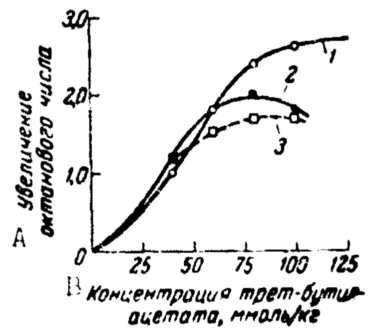


Fig. 5.19. Comparative data on effectiveness of *tert*-butyl acetate according to various octane-rating methods [34]: 1) research; 2) motor; 3) road. A) Octane number increase; B) concentration of *tert*-butyl acetate, mmole/kg.

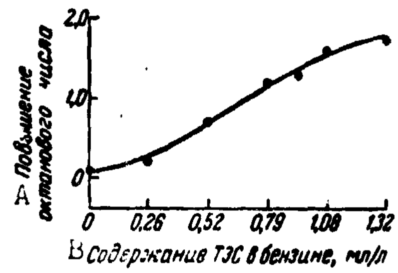


Fig. 5.20. Influence of TEL concentration in gasoline on octane number increase on addition of 0.7% *tert*-butyl acetate [37]. A) Octane number increase; B) TEL content in gasoline, ml/liter.

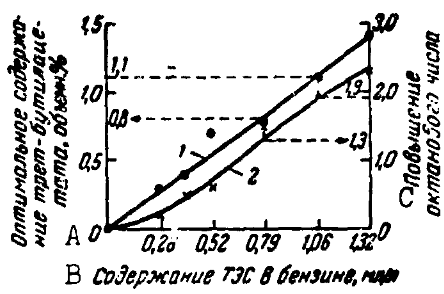


Fig. 5.21. Influence of TEL concentration in gasoline [37] on increase in octane rating and optimum *tert*-butyl acetate concentration: 1) optimum *tert*-butyl acetate content; 2) increase in octane rating on addition of optimum amount of *tert*-butyl acetate. A) Optimum *tert*-butyl acetate content, % by volume; B) TEL content in gasoline, ml/liter; C) octane number increase.

TABLE 5.21

Effectiveness of *tert*-Butyl Acetate as a Function of Engine Crankshaft Speed [36]

1 Число оборотов	2 Дорожное октановое число		
	3 без присадки	4 с трет-бутилацетатом (0,5% объемн.)	5 Увеличение октанового числа при добавлении присадки
1000	94,7	95,1	0,4
2250	91,8	92,3	0,5
2500	90,6	92,1	1,5
3000	90,2	91,9	1,7

1) Revolutions per minute
2) Road octane rating
3) Without additive
4) With *tert*-butyl acetate (0.5% by volume)
5) Octane number increase due to additive.

TABLE 5.22

Influence of *tert*-Butyl Acetate Concentration on Octane Number (Motor) [36] of Leaded Fuels (0.8 ml of TEL to 1 liter of Fuel)

1 Концентрация присадки	2 Базовый бензин		5 Базовый бензин + 25% алкилата	
	3 Октановое число	4 Увеличение октанового числа	3 Октановое число	4 Увеличение октанового числа
0,0	88,7	—	91,7	—
0,25	89,6	0,9	92,5	0,8
0,50	90,0	1,3	93,3	1,6
1,00	90,2	1,5	93,2	1,5

1) Additive concentration
2) Base gasoline
3) Octane rating
4) Octane rating increase
5) Base gasoline + 25% alkylate.

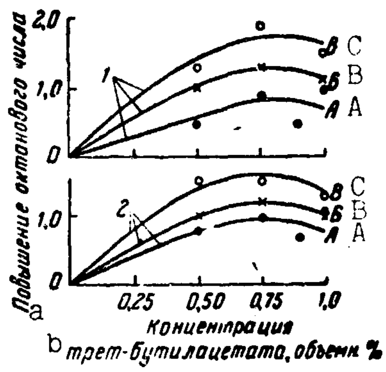


Fig. 5.22. Influence of *tert*-butyl acetate concentration on octane rating increase of automotive gasolines [37]: 1) research; 2) motor; A) 100-octane gasoline; B) 102-octane gasoline; C) 105.5-octane gasoline. a) Increase in octane rating; b) *tert*-butyl acetate concentration, % by volume.

they have rather broad concentration ranges corresponding to the maximum effect.

Tert-butyl acetate is a colorless liquid that mixes well with gasolines in any proportions [35]. This compound and its gasoline solutions are stable, nontoxic, noncorrosive, compatible with other additives; they do not damage paint coatings, rubber, etc.

Below we list the physical properties of *tert*-butyl acetate [35]:

Formula.................................. $CH_3-\underset{\underset{O}{\|}}{C}-O\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

Molecular weight........................... 116

Temperatures, °C

boiling point............................ 96

flash point (closed crucible)............ below 0

cloud point..................................	below -60
melting point................................	below -60
Density ρ_4^{20}..................................	0.866
Refractive index n_4^{20}........................	1.3870
Solubility in water at 26.7°C, %............	0.62

The largest increase in octane rating resulting from addition of *tert*-butyl acetate is observed when antiknock stability is rated by the research method (Fig. 5.19).

Under road conditions, the effectiveness of *tert*-butyl acetate depends on engine operating conditions (Table 5.21); the optimum concentration in the gasoline depends on the latter's composition (Table 5.22). It averages 0.75% by volume [37].

The effectiveness of *tert*-butyl acetate increases with increasing TEL concentration in the gasoline (Fig. 5.20) and with increasing octane rating of the base gasoline (Fig. 5.22). Here the optimum concentration of the ester, that which ensures the largest octane-rating increase, also increases (Fig. 5.21).

At the present time, *tert*-butyl acetate, bearing the tradenames TLA or "Octagen," is used in the USA to enhance the antiknock stability of leaded premium automotive gasolines. The raw materials for production of *tert*-butyl acetate (isobutylene and acetic acid) are not critical, and its production presents no difficulty.

Manganese antiknocks

The high antiknock effectiveness of certain manganese compounds was first reported in 1957 [38, 39]. High antiknock properties [40, 41] were also observed for manganese methylcyclopentadienyltricarbonyl [MMCT] (МЦТМ), manganese cyclopentadienyltricarbonyl [MCT] (ЦТМ) and manganese pentacarbonyl [MPC] (ПКМ).

At normal temperatures, MCT and MPC are solid crystalline substances, while MMCT is a transparent low-viscosity liquid with a light amber color and faint grassy odor [42, 43].

As regards effectiveness (Table 5.23) and behavior in various gasolines, MCT and MMCT are quite similar [44].

The antiknock effectiveness of magnesium additives introduced into individual hydrocarbons and gasolines of various compositions is shown in Tables 5.24 and 5.25 and Fig. 5.23.

The receptiveness of gasolines to manganese antiknocks depends on the chemical composition of the gasolines (see Table 5.24): with increasing paraffinic content and decreasing aromatic content, the gasolines become more receptive. Alkylates, gas gasolines, C_5-C_6 isomers, etc., show high receptivity to manganese antiknocks. The highest effectiveness of manganese antiknocks is observed when they are introduced into A-56 and A-66 gasolines. Introduction of equal quantities of TEL and MCT has about the same effect. In evaluating the comparative effectiveness of TEL and

manganese antiknocks in terms of the equivalent quantities of metal introduced into the gasoline with the antiknocks, manganese is found to be more effective than lead (see Table 5.25).

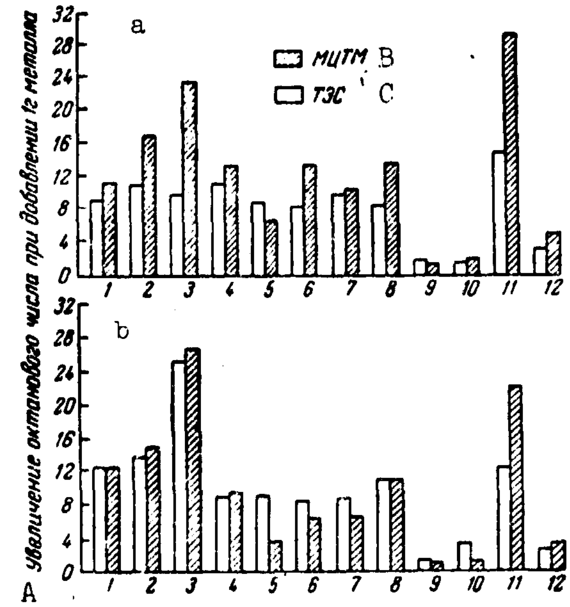


Fig. 5.23. Receptiveness of pure hydrocarbons to MMCT and TEL [6]: a) research octane numbers; b) motor octane numbers; 1) 2,2-dimethylbutane; 2) 2-methylpentane; 3) *n*-heptane; 4) 2,4-dimethylpentane; 5) triptane; 6) 2,2,4-trimethylpentane; 7) cyclohexane; 8) methylcyclohexane; 9) 2-methylbutene-2; 10) diisobutylenes; 11) octene-1; 12) ethylbenzene. A) Increase in octane rating on addition of 1 g of metal; B) MMCT; C) TEL.

TABLE 5.23

Effectiveness of MCT and MMCT (According to A.A. Gureyev and A.P. Zarubin)

1 Топливо	2 = Октановое число, моторный метод			7 Октановое число, исслед. метод		
	3 без присадок	4 с присадкой, 1 г/кг		3 без присадок	4 с присадкой, 1 г/кг	
		5 ЦТМ	6 МЦТМ		5 ЦТМ	6 МЦТМ
8 Смесь 60% изооктана + 40% гептана	60,0	72,1	71,8	—	—	—
9 Смесь 40% толуола + 30% гептана + 20% диизобутилена + 10% изооктана	77,8	82,2	81,9	87,0	95,1	95,1
10 Бензин каталитического риформинга	70,6	78,5	78,3	74,8	83,4	83,1
11 Бензин каталитического крекинга	72,0	76,9	77,0	78,0	85,9	86,3

1) Fuel
2) Motor octane number
3) Without additives
4) With additive, 1 g/kg
5) MCT
6) MMCT
7) Research octane number
8) Mixture of 60% isooctane + + 40% heptane
9) Mixture of 40% toluene + + 30% heptane + 20% diisobutylene + 10% isooctane
10) Catalytic-reforming gasoline
11) Catalytic-cracking gasoline.

TABLE 5.24

Influence of Antiknocks on Octane Ratings of Commercial Gasolines and Their Components [45]

1 Бензин	2 Октановое число без антидетонатора		5 Октановое число при добавлении антидетонатора											
			6 ТЭС, г/кг						7 ЦТМ, г/кг					
			0,41		0,82		1,23		0,5		1,0		1,5	
	3 м. м.*	4 и. м.*	м. м.	и. м.	м. м.	и. м.	м. м.	и. м.	м. м.	и. м.	м. м.	и. м.	м. м.	и. м.
А-56	58,3	59,6	62,7	63,6	67,6	69,0	70,2	72,0	66,2	69,5	69,6	72,5	71,8	74,6
А-66	64,5	66,7	69,1	71,3	72,2	74,1	74,0	76,9	70,8	73,5	74,3	77,7	76,5	80,5
А-72	74,1	77,9	78,1	82,5	80,6	85,1	81,8	87,2	79,0	84,5	81,1	86,9	81,8	88,9
8 Прямой перегонки	64,3	65,3	72,0	70,8	76,8	76,4	—	—	71,7	73,4	75,5	75,4	79,5	80,5
9 Термического крекинга	68,6	73,2	71,8	77,8	74,0	80,2	75,1	81,7	73,2	80,7	74,7	83,3	75,8	84,6
10 Каталитического крекинга	74,7	80,7	77,9	84,8	79,8	87,3	80,9	89,1	78,1	85,9	79,3	87,8	79,4	89,0
11 Каталитического риформинга	75,0	78,9	80,9	85,6	82,8	89,9	85,3	93,3	79,1	85,4	81,1	87,3	82,0	89,1

*M.m. stands for the motor method and i.m. for the research method of determining gasoline octane ratings.

1) Gasoline
2) Octane number without antiknock
3) m.m.*
4) i.m.*
5) Octane rating on addition of antiknock
6) TEL, g/kg
7) MCT, g/kg
8) Straight-run
9) Thermal-cracking
10) Catalytic-cracking
11) Catalytic-reforming.

TABLE 5.25

Average Receptiveness of Automotive Gasolines to Antiknocks (MMCT and TEL), Calculated on the Basis of Determinations for 24 Specimens of High-Octane Gasolines [43]

1 МЦТМ, г Mn на 1 л	2 Октановое число, исслед. метод	3 ТЭС, г Pb на 1 л	2 Октановое число, исслед. метод
0	92,0	0	92,0
0,066	95,1	0,066	93,6
0,132	96,3	0,132	94,7
0,264	97,8	0,264	96,1
0,529	99,6	0,529	97,7
		0,792	98,7

1) MMCT, g of Mn to 1 liter
2) Research octane number
3) TEL, g of Pb to 1 liter.

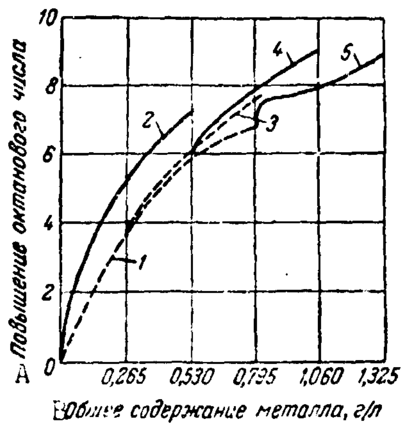


Fig. 5.24. Increase in gasoline octane numbers on combined addition of MMCT and TEL [6]: 1) TEL alone; 2) MMCT alone; 3) TEL + + MMCT; 4) 2TEL + MMCT; 5) 3TEL + MMCT. A) Octane number increase; B) total metal content, g/liter.

The sensitivity of manganese antiknocks to engine operating conditions (difference between research and motor octane ratings) is somewhat greater than that of TEL; thus the research method usually indicates higher effectiveness of manganese antiknocks than the motor method (Fig. 5.24).

The amount and nature of sulfur compounds in the gasolines have less influence on receptivity to manganese antiknocks than that to TEL (Tables 5.26 and 5.27).

Manganese antiknocks sharply increase the detonation stability of gasolines containing TEL. The first portions are particularly effective (Table 5.28). The greater the amount of TEL in the gasoline, the greater will be the effect of a manganese anti-

TABLE 5.26

Influence of Sulfur-Organic Compounds on Receptivity of Hydrocarbon Mixture (40% Toluene, 30% Heptane, 20% Diisobutylene and 10% Isooctane) to Manganese Antiknock and TEL [9]

1 Сероорганическое соединение, добавленное к смеси	2 Количество серы, %	3 Количество антидетонатора, г/кг		6 Моторный метод		9 Исслед. метод	
		4 ТЭС	5 ЦТП	7 октановое число	8 увеличение октанового числа	7 октановое число	8 увеличение октанового числа
10 Бензилмеркаптан	0,0	0,82	—	83,9	—	95,3	—
»	0,005	0,82	—	83,3	0,6	95,0	0,3
	0,02	0,82	—	82,2	1,7	84,7	0,6
	0,05	0,82	—	81,4	2,5	93,8	1,5
	0,0	—	0,8	80,4	—	94,1	—
	0,005	—	0,8	80,1	0,3	93,4	0,7
	0,02	—	0,8	80,4	0,0	93,4	0,7
	0,05	—	0,8	80,3	0,1	93,9	0,2
11 Диэтилсульфид	0,0	0,82	—	83,9	—	95,3	—
»	0,005	0,82	—	83,5	0,4	95,0	0,3
	0,02	0,82	—	83,4	0,5	94,8	0,5
	0,05	0,82	—	81,9	2,0	93,6	1,7
	0,0	—	0,8	80,4	—	94,1	—
	0,005	—	0,8	80,4	0,0	94,2	+0,1
	0,02	—	0,8	80,4	0,0	94,1	0,0
	0,05	—	0,8	80,3	0,1	94,3	+0,2
12 Дибутилсульфид	0,0	0,82	—	83,9	—	95,3	—
»	0,005	0,82	—	83,6	0,3	94,9	0,4
	0,02	0,82	—	82,5	1,4	94,4	0,9
	0,05	0,82	—	31,2	2,7	93,8	1,5
	0,0	—	0,8	80,4	—	94,1	—
	0,005	—	0,8	80,2	0,2	94,5	+0,4
	0,02	—	0,8	80,7	+0,3	94,3	+0,2
	0,05	—	0,8	80,4	0,0	94,2	+0,1

1) Sulfur-containing compound added to mixture
2) Amount of sulfur, %
3) Amount of antiknock, g/kg
4) TEL
5) MCT
6) Motor
7) Octane number
8) Octane number increase
9) Research
10) Benzylmercaptan
11) Diethyl sulfide
12) Dibutyl sulfide.

knock (see Fig. 5.24). This "promoting" action of manganese on the antiknock effectiveness of TEL is utilized in the USA in the new AK-33Mix additive, which consists of TEL and MMCT in the proportions 0.052 g of Mn to 1 ml of TEL [47, 48].

Under use conditions, the effectiveness of manganese antiknocks [49, 50] is higner than indicated by the motor octane number (Fig. 5.25 and Table 5.29).

The influence of manganese antiknock (MCT) on deposit buildup is shown in Tables 5.30-5.33.

When scavengers are added to manganese antiknocks, the total amount of deposits formed is reduced (see Table 5.33) and spark-plug operation improved. The amount of deposits [51] formed in the intake manifold of an IT-9-2 engine using gasolines with MCT is smaller than when TEL gasolines are used (see Table 5.31).

The deposit formed on combustion of gasolines with manganese antiknocks contributes to surface ignition. Its frequency is practically directly proportional to the MCT concentration in the gasoline (Fig. 5.26). An effective way to lower the incidence of surface ignition in engine operation on gasolines with MCT is to add tricresyl phosphate to the gasoline. The optimum concentration of this substance, that necessary to convert the manganese in the fuel to the orthophosphate, is 0.2% of the theoretical amount (Fig. 5.27).

TABLE 5.27

Influence of Sulfur-Organic Compounds on Receptivity [9] of a Mixture of Hydrocarbons (56% Isooctane + 44% Heptane) to Manganese Antiknock and TEL*

1 Сероорганическое соединение, добавленное к смеси	2 Количество серы, %	3 ТЭС 0,82 г/кг		6 ЦТМ 0,8 г/кг	
		4 октановое число	5 уменьшение октанового числа	4 октановое число	5 уменьшение октанового числа
7 Смесь, не содержащая серы	0,0	72,4	—	67,9	—
8 Бензилмеркаптан	0,05	64,7	7,7	65,0	2,9
9 Пропилмеркаптан	0,035	68,1	4,3	65,6	2,3
10 Изоамилмеркаптан	0,05	67,3	5,1	65,3	2,6
11 втор-Октилмеркаптан	0,05	65,4	7,0	65,4	2,5
12 Диэтилсульфид	0,05	67,2	5,2	65,7	2,2
13 Диизоамилсульфид	0,05	66,5	5,9	65,4	2,5
14 Дибутилдисульфид	0,05	65,0	7,4	66,5	1,4
15 Тиофан	0,05	67,5	4,9	66,2	1,7

*Octane numbers determined by motor method.

1) Sulfur-organic compound added to mixture
2) Amount of sulfur, %
3) TEL, 0.82 g/kg
4) Octane number
5) Octane number decrease
6) MCT, 0.8 g/kg
7) Mixture without sulfur
8) Benzylmercaptan
9) Propylmercaptan
10) Isoamylmercaptan
11) *sec*-octylmercaptan
12) Diethyl sulfide
13) Diisoamyl sulfide
14) Dibutyl disulfide
15) Thiophane.

TABLE 5.28

Receptiveness of Leaded Gasolines and Their Components to MMCT [43]

1 Образцы	2 Октановое число, исслед. метод		5 Повышение октанового числа с 0,8 мл ТЭС на 1 л и МЦТМ, г/л			
	3 без ТЭС	4 с 0,8 мл ТЭС на 1 л топлива	0,033	0,066	0,132	0,265
6 Алкилат	93,8	104,7	6,6	7,5	9,2	11,3
7 Газовый бензин	71,0	88,0	2,9	4,2	5,0	5,8
8 Изомеры C_5-C_6	85,0	97,0	4,6	5,0	5,8	7,4
9 Средний бензин						
10 обычного сорта	83,7	93,6	1,6	2,0	2,2	2,9
11 премиального сорта	91,6	98,5	0,5	0,7	1,1	1,8

1) Specimen
2) Research octane number
3) Without TEL
4) With 0.8 ml of TEL to 1 liter of fuel
5) Increase in octane number with 0.8 ml of TEL to 1 liter and ... g/liter of MMCT
6) Alkylate
7) Gas gasoline
8) C_5-C_6 isomers
9) Average gasoline
10) Regular
11) Premium.

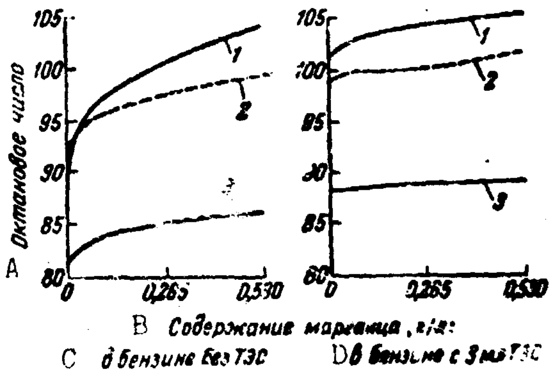


Fig. 5.25. Increase in octane numbers of gasolines on addition of MMCT in pure form and together with TEL in rating by laboratory methods and on full-scale single-cylinder engine [6]: 1) full-scale single-cylinder engine; 2) research; 3) motor. A) Octane number; B) manganese content, g/liter; C) in gasoline without TEL; D) in gasoline with 3 ml of TEL.

TABLE 5.29

Effectiveness of Magnesium Antiknocks under Road Conditions [49, 50]

1 Топливо	2 ТЭС мл/л	3 Марганец г/л	4 Октановое число		7 Дорожное октановое число (измененный метод оценки по кривым затухания детонации) при различных скоростях вращения коленчатого вала				
			5 исслед. метод	6 моторный метод	8 1500 об/мин	2000 об/мин	2500 об/мин	3000 об/мин	9 Среднее
А	0	0	90,7	73,5	90,1	90,6	90,8	89,9	90,4
		0,066	94,4	82,4	93,2	93,5	93,8	92,2	93,2
		0,132	95,7	83,3	94,5	95,0	94,4	93,2	94,3
		0,264	97,3	83,7	95,5	96,5	95,9	94,9	95,7
		0,528	99,2	85,0	97,4	98,0	97,6	96,8	97,5
	0,792	0	98,0	85,2	96,0	96,8	96,2	95,9	96,0
		0,026	98,8	86,0	94,6	97,6	97,4	96,5	97,0
		0,066	98,9	86,2	96,6	97,6	97,3	96,5	97,0
		0,132	99,4	86,5	97,3	97,7	97,6	96,8	97,3
		0,264	100,0	87,0	97,3	97,9	97,6	96,7	97,4
10 Б	0	0	90,6	83,0	88,3	89,6	89,9	89,7	89,4
		0,066	94,1	84,6	89,8	92,5	93,7	93,3	92,3
		0,132	95,7	85,3	92,9	94,2	95,4	94,8	94,3
		0,264	97,7	86,5	94,8	96,4	97,8	97,0	96,5
		0,528	99,6	88,2	97,0	98,9	99,4	99,0	98,6
	0,792	0	99,0	90,7	97,1	99,1	99,4	99,5	98,8
		0,026	99,3	90,6	96,4	99,0	99,9	99,7	98,8
		0,066	99,5	91,0	97,5	99,9	100,6	100,4	99,6
		0,132	99,7	91,0	96,8	99,4	100,3	99,8	99,1
		0,264	100,8	91,3	97,9	100,0	100,8	99,9	99,7

1) Fuel
2) TEL, ml/liter
3) Manganese, 'liter
4) Octane number
5) Research
6) Motor
7) Road octane number (modified method of rating from detonation decay curves) at ' ious crankshaft speeds
8) .) rev/min
9) Average 10) B.

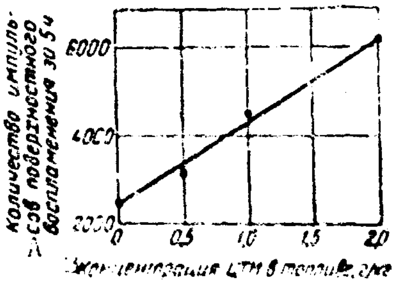


Fig. 5.26. Influence of MCT concentration in gasoline on surface ignition [44]. A) Number of surface-ignition impulses in 5 h; B) MCT concentration in fuel, g/kg.

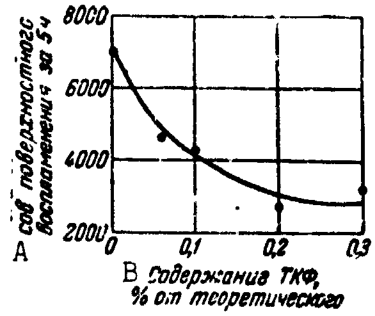


Fig. 5.27. Influence of tricresyl phosphate concentration (in fractions of quantity theoretically necessary for conversion of all manganese to the orthophosphate) on surface ignition [44]. A) Number of surface-ignition pulses in 5 h; B) TCP (ТКФ) content, % of theoretical.

TABLE 5.30

Influence of Antiknock Content [44] in A-72 Gasoline on Deposit Formation in Engine of IT-9-2 Machine*

1 Антидетонатор, добавленный к бензину	2 Количество нагара (в мг) при концентрации антидетонатора, г/кг				
	3 без антидетонатора	0,27	0,54	1,00	1,50
4 Тетраэтилсвинец	2,0	7,4	8,8	12,7	14,6
5 Циклопентадиенилтрикарбонилмарганец	2,0	5,0	7,2	10,4	12,8

*4-hour test. Deposit buildup on special collector valve.

1) Antiknock used in gasoline
2) Amount of deposits (in mg) at antiknock concentration of ..., g/kg
3) No antiknock
4) Tetraethyllead
5) Manganese cyclopentadienyltricarbonyl.

TABLE 5.31

Influence of Antiknock Content [44] in A-66 Gasoline on Deposit Buildup in ZIL-120 Engine and on Deposits in Intake System of IT-9-2 Tester Engine

1 Бензин	2 Нагарообразование, мг/ч	3 Количество отложений во впускной системе, мг/ч
4 Исходный	26	25
5 То же + антидетонатор:		
6 1 мл Р-9 на 1 кг	42	41
7 0,8 г ЦТМ на 1 кг	31	33

1) Gasoline
2) Deposit buildup, mg/h
3) Amount of deposits in intake system, mg/h
4) Initial
5) Same + antiknock
6) 1 ml of R-9 to 1 kg
7) 0.8 g of MCT to 1 kg.

TABLE 5.32

Influence of Amount of MCT in Gasoline on Deposit Buildup in Engine and on Deposits in Intake System of Test Engine [44]

1 Бензин	2 Нагарообразование, мг/ч		5 Количество отложений во впускной системе, мг/ч	
	3 на бензине А-56	4 на бензине Б-70	3 на бензине А-56	4 на бензине Б-70
6 Исходный	22	9	11,0	10,0
7 То же + ЦТМ, г/кг:				
0,2	22	16	12,0	11,0
0,4	22	17	19,0	11,0
0,8	30	25	21,0	11,0

1) Gasoline
2) Deposit formation, mg/h
3) A-56 gasoline
4) V-70 gasoline
5) Amount of deposits in intake system, mg/h
6) Initial
7) Same + MCT, g/kg.

TABLE 5.33

Amount of Deposits [44] Formed in "Moskvich-407" Engine over 400 hr of Testing on A-66 Gasoline with Various Antiknocks

1 Антидетонаторы	2 Количество нагара, г				
	3 днище поршня	4 головка цилиндра	5 выпускной клапан	6 впускной клапан	7 всего
8 0,8 г ЦТМ на 1 кг без выносителя	6,40	7,20	0,40	0,40	14,40
9 0,82 г ТЭС на 1 кг с выносителем (бромистый этил)*	5,65	6,00	5,65	2,50	19,80
10 0,8 г ЦТМ на 1 кг с бромистым этилом	4,38	4,84	1,64	0,41	11,29
11 0,8 г ЦТМ на 1 кг с бис-этилксантогеном	4,84	4,45	0,39	0,35	10,03

*The test time for the leaded gasoline was 330 h.

1) Antiknock
2) Amount of deposits, g
3) Top of piston
4) Cylinder head
5) Exhaust valve
6) Intake valve
7) Total
8) 0.8 g of MCT to 1 kg without scavenger
9) 0.82 g of TEL to 1 kg with scavenger (ethyl bromide)*
10) 0.8 g of MCT to 1 kg with ethyl bromide
11) 0.8 g of MCT to 1 kg with *bis*-ethylxanthogen.

TABLE 5.34

Stability of Hydrocarbon Solutions of MCT during Storage in Light [44]

1 Топливо	2 Цвет	3 Оптическая плотность относительно дистиллированной воды на ФЭК-М с синим светофильтром	4 Поведение образца при хранении в стеклянной посуде при дневном свете
5 Изооктан + 0,8 г ЦТМ на 1 кг	6 Бесцветный	0,00	7 Через 6 ч выпал обильный хлопьевидный осадок
8 Изооктан + 0,8 г ЦТМ на 1 кг + 0,1% пиролизата	9 То же	0,01	10 Через 24 ч образец помутнел и выпал осадок
11 Бензол + 0,8 г ЦТМ на 1 кг	»	0,00	Выпал обильный осадок 12 через 48 ч
13 Бензол + 0,8 г ЦТМ на 1 кг + 0,1% пиролизата	»	0,01	14 Выпал осадок через 48 ч
15 Бензол + 0,8 г ЦТМ на 1 кг + 0,01 г/кг судана желтого	16 Желтый	0,24	17 Образец помутнел через 96 ч
18 Бензол + 0,8 г ЦТМ на 1 кг + 0,01 г/кг судана красного	19 Красный	0,24	9 То же
20 Бензин А-66 + 0,8 г ЦТМ на 1 кг	21 Соломенно-желтый	0,05	22 Бензин помутнел через 240 ч
23 Бензин А-72 + 0,8 г ЦТМ на 1 кг	9 То же	0,07	9 То же
24 Бензин Б-70 + 0,8 г ЦТМ на 1 кг	25 Слабо-желтый	0,02	26 Бензин помутнел через 72 ч

1) Fuel
2) Color
3) Optical density with respect to distilled water on FEK-M with blue filter
4) Behavior of specimen during storage in glass vessel in daylight
5) Isooctane + 0.8 g of MCT to 1 kg
6) Colorless
7) Heavy flocculent precipitate after 6 h
8) Isooctane + 0.8 g of MCT to 1 kg + 0.1% pyrolyzate
9) Same
10) Specimen turbid, with precipitate, after 24 h
11) Benzene + 0.8 g of MCT to 1 kg
12) Heavy precipitate after 48 h
13) Benzene + 0.8 g of MCT to 1 kg + 0.1% pyrolyzate
14) Precipitate after 48 h

15) Benzene + 0.8 g of MCT to 1 kg + 0.01 g/kg of Sudan yellow
16) Yellow
17) Specimen turbid after 96 hr
18) Benzene + 0.8 g of MCT to 1 kg + 0.01 g/kg of Sudan red
19) Red
20) A-66 gasoline + 0.8 g of MCT to 1 kg
21) Straw yellow
22) Gasoline cloudy after 240 hr
23) A-72 gasoline + 0.8 g of MCT to 1 kg
24) B-70 gasoline + 0.8 g of MCT to 1 kg
25) Faint yellow
26) Gasoline cloudy after 72 hr.

While the addition of manganese antiknocks does not change the color of gasolines, gasoline color does have an influence on the chemical stability of MCT in hydrocarbon solutions when they are exposed to sunlight (Table 5.34). Addition of MCT is not detrimental to the low-temperature properties of automotive gasolines, nor does it increase their acidity; the amount of existent gums is found to be somewhat higher (2-4 mg to 100 ml). The corrosive aggressiveness of gasolines with MCT is approximately the same as that of gasolines containing R-9 ethyl fluid (Table 5.35); the chemical stability of gasolines is lowered by addition of MCT. Vigorous absorption of oxygen with a simultaneous increase in the content of peroxide compounds, existent gums and organic acids is observed much earlier in the oxidation of cracking-gasoline with antioxidants in the presence of MCT.

Other metal-organic antiknocks

Among the other metal-organic compounds, certain compounds containing iron, copper, cobalt, chromium, potassium, tellurium, thallium, and others have high antiknock properties. Most thoroughly studied as antiknock additives are compounds of iron and copper: iron pentacarbonyl [IPC] (ПКЖ), iron dicyclopentadienyl (ferrocene), and chelate copper salts. The physical properties of iron-organic antiknocks are listed in Table 5.36.

The effectiveness of IPC as an antiknock is 15-20% lower than that of TEL (Table 5.37). IPC was used abroad at one time, but then production was stopped [53-55]. During the '40's, extensive tests of IPC were conducted in the USSR [56-60] to determine its usefulness as an antiknock additive to kerosenes (Table 5.38); it did not come into use as an antiknock additive because the iron oxide formed on combustion of IPC was deposited in combustion chambers and increased engine wear. No scavengers have been found for the combustion products of IPC.

The effectiveness of ferrocene is about the same as that of IPC (Table 5.39) [61]. It is preserved even when it is added to leaded gasolines (Table 5.40). However, the lack of effective scavengers for the iron oxide is an obstacle to the extensive use of ferrocene.

Chelate copper salts [62] are characterized by rather high

TABLE 5.35

Influence of MCT and TEL on Physicochemical Properties of Automotive Gasolines [44]

1 Показатели	2 Исходный бензин	3 Бензин с 1 мл Р-9 на 1 кг	4 Бензин с 0,8 г ЦТМ на 1 кг
5 Кислотность, мг КОН на 100 мл	0,93	0,94	0,93
6 Фактические смолы, мг на 100 мл	4	7	6
7 Коррозия, мг/м² (испытание на стальной пластинке*):			
8 в газовой фазе	0,4	0,5	0,6
9 в жидкой фазе	0,4	0,7	0,8
10 Химическая стабильность: без антиокислителей, фактические смолы после окисления**, мг на 100 мл:			
11 без металла	8	10	11
12 с медью	45	42	43
13 со сталью	9	12	12
14 с антиокислителями, длительность индукционного периода окисления, мин			
15 с пиролизатом (0,05%)	310	—	230
16 n-оксидифениламином (0,005%)	170	—	130
17 с ионолом (0,05%)	385	—	210

*Test for 10 h at 75°C.
**Oxidation for 2 h at 110°C.

1) Index
2) Original gasoline
3) Gasoline with 1 ml of R-9 to 1 kg
4) Gasoline with 0.8 g of MCT to 1 kg
5) Acidity, mg of KOH to 100 ml
6) Existent gums, mg to 100 ml
7) Corrosion, mg/m² (steel plate test*)
8) In gaseous phase
9) In liquid phase
10) Chemical stability without antioxidants, existent gums after oxidation,** mg per 100 ml
11) Without metal
12) With copper
13) With steel
14) With antioxidants, length of oxidation-induction period, min
15) With pyrolyzate (0.05%)
16) p-hydroxydiphenylamine (0.005%)
17) With ionol (0.05%).

TABLE 5.36

Physical Properties of Iron-Organic Antiknocks [6, 14, 52]

1 Показатели	2 Пентакарбонил железа	3 Дициклопентадиенилжелезо (ферроцен)
4 Формула	6 $Fe(CO)_5$	7 $Fe(C_5H_5)_2$
5 Физическое состояние и цвет	Жидкость бледно-желтого цвета	Желтые кристаллы
8 Плотность, ϱ_4^{20}	1,457	—
9 Температура, °C:		
10 кипения	102,5	249
11 плавления	—21	+174
12 Растворимость:		
13 в углеводородах	14 Хорошая	
15 в воде	16 Не растворяется	
17 Токсичность	18 Не токсичен	

1) Index
2) Iron pentacarbonyl
3) Iron dicyclopentadienyl (ferrocene)
4) Formula
5) Physical state and color
6) Pale yellow liquid
7) Yellow crystals
8) Density
9) Temperatures, °C
10) Boiling point
11) Melting point
12) Solubility
13) In hydrocarbons
14) Good
15) In water
16) Insoluble
17) Toxicity
18) Nontoxic.

TABLE 5.37

Effectiveness of IPC and TEL (According to D.S. Stasinevich, K.N. Fastovoy and A.L. Gol'dshteyn)

1 Топливо	2 Октановое число чистого топлива	3 Октановое число топлива с добавкой							
		4 ПКЖ, мл/кг				5 Р-9, мл/кг			
		0,5	1,0	1,5	2,0	0,5	1,0	1,5	2,0
6 40% изооктана + 60% н-гептана	40,0	48,0	54,2	61,6	64,0	50,0	61,8	67,8	71,0
7 50% изооктана + 50% н-гептана	50,0	56,0	63,2	67,0	70,7	61,0	70,0	73,6	76,2
8 60% изооктана + 40% н-гептана	60,0	66,0	72,2	76,8	79,5	70,4	77,0	79,6	81,0
9 Автомобильные бензины товарные:									
№ 1	57,6	63,0	66,8	68,5	—	65,0	67,8	—	72,3
№ 2	58,4	62,0	66,0	69,0	—	—	67,0	—	72,4
№ 3	55,0	58,4	59,3	66,0	—	—	—	68,8	—
№ 4	55,0	56,8	60,8	62,3	65,4	—	—	65,7	—
№ 5	53,7	58,8	60,3	63,2	—	62,3	66,0	68,4	—
10 Автомобильные бензины прямогонные:									
№ 1	56,4	63,0	67,4	71,4	73,4	—	—	72,1	—
№ 2	54,8	61,8	66,7	69,9	73,0	—	—	—	—
№ 3	56,0	61,5	68,4	73,0	76,0	64,8	70,5	75,0	76,0
11 Авиационный бензин Б-70, № 1	68,0	73,8	77,0	79,0	81,0	—	80,5	—	83,0

1) Fuel
2) Octane number of pure fuel
3) Octane number of fuel with additive
4) IPC, ml/kg
5) R-9, ml/kg
6) 40% isooctane + 60% *n*-heptane
7) 50% isooctane + 50% *n*-heptane
8) 60% isooctane + 40% *n*-heptane
9) Commercial automotive gasolines
10) Straight-run automotive gasolines
11) B-70 aviation gasoline, No. 1.

TABLE 5.38

Antiknock Effect of Adding IPC to Tractor Kerosenes [56, 57]

A Керосин	B Октановое число при добавлении ПКЖ, мл/л				
	0	2	4	6	8
C Бакинский:					
D образец 1	34	44	55	—	69
образец 2	42	49	57	64	68
E Грозненский	9	18	28	33	42
F Майкопский	29	33	42	50	57

A) Kerosene
B) Octane number on addition of IPC, ml/liter
C) Baku
D) Specimen ...
E) Groznyy
F) Maykop.

TABLE 5.39

Antiknock Effectiveness of IPC and Ferrocene [61] on Addition to 60-Octane Gasoline

1 Присадки	2 Содержание присадки, %	3 Октановое число	1 Присадки	2 Содержание присадки, %	3 Октановое число
4 Пентакарбонил железа (ПКЖ)	0,056	64,4	5 Дициклопентадиенилжелезо (ферроцен)	0,058	[illegible]
	0,112	69,1		0,106	71,6
	0,202	76,2		0,192	75,2
	0,335	82,7		0,319	79,5

1) Additive
2) Additive content
3) Octane number
4) Iron pentacarbonyl (IPC)
5) Iron dicyclopentadienyl (ferrocene).

TABLE 5.40

Combined Antiknock Effectiveness of TEL and Iron-Organic Antiknocks [61]

1 Содержание			5 Октановое число
2 ТЭС в бензине, г/л	3 железоорганического антидетонатора в бензине, г/л	4 железа в бензине, г/л	
0,0	0,0	0,0	77,2
6 Ферроцен			
0,0	0,88	0,264	87,3
0.0	1,76	0,528	89,7
0,0	2,64	0,792	91,2
0,28	0,88	0,264	90,8
0,28	1,76	0,528	93,1
0,28	2,64	0,792	94,6
6 Ферроцен			
0,56	0.0	0,0	88,4
0,56	0,88	0,264	92,4
0,56	1,76	0.528	95,4
0,56	2,64	0,792	96,0
7 ПКЖ			
0,0	0,92	0,264	87,9
0,0	1,85	0,528	92,4

1) Content
2) TEL in gasoline, g/liter
3) Iron-organic antiknock in gasoline, g/liter
4) Iron in gasoline, g/liter
5) Octane number
6) Ferrocene
7) IPC.

TABLE 5.41

Detonation Stability of Gasolines with Addition of Aminomethylene Ketone Copper Derivatives (According to F.B. Ashbel' et al.)

1 Аминометиленкетоны, медные производные которых добавлялись в бензин	2 Октановое число при добавлении медных производных, моль/кг						
	0,0025	0,01	0,016	0,01	0,016	0,01	0,016
	3 бензина Б-70 (о. ч. = 69,2)			4 автомобильного бензина (о. ч. = 61,6)		5 смеси изооктана и гептана (о. ч. = 55)	
6 1-Метиламинобутен-1-он-3 (метиламинометиленацетон)	72,0	78,0	79,6	69,6	71,5	66,4	70,2
7 1-Этиламинобутен-1-он-3	73,1	79,0	80,4	71,4	71,8	67,6	71,2
8 1-Метиламинопентен-1-он-3	70,5	76,5	80,1	68,4	—	64,4	—
9 1-Метиламиногексен-1-он-3	71,6	77,6	79,2	68,2	—	—	—
10 1-Метиламино-5-метилгексен-1-он-3 (метиламинометиленизопропилацетон)	71,6	77,2	79,2	68,4	69,7	65,6	66,4
11 1-Метиламино-4,4-диметилпентен-1-он-3	72,4	77,7	79,5	69,0	70,5	65,6	68,0
12 1-Метиламинооктен-1-он-3	71,6	77,5	—	68,0	—	65,0	—
13 1-Этиламино-5-метилгексен-1-он-3	72,0	77,5	79,2	69,1	70,0	65,6	66,4
14 1-Изопропиламино-5-метилгексен-1-он-3	71,4	77,4	79,4	68,2	70,2	—	65,6
15 2-Метиламино[illegible]-2-он-4	71,2	75,2	—	—	—	64,3	—

1) Aminometh[illegible]one whose copper derivative was added to the gasol[illegible]

2) Octane number after addition of ... mole/kg of copper derivatives
3) B-70 gasoline (69.2-octane)
4) Automotive gasoline (61.6-octane)
5) Mixture of isooctane and heptane (55-octane)
6) 1-Methylaminobutene-1-one-3 (methylaminomethylene acetone)
7) 1-Ethylaminobutene-1-one-3
8) 1-Methylaminopentene-1-one-3
9) 1-Methylaminohexene-1-one-3
10) 1-Methylamino-5-methylhexene-1-one-3 (methylaminomethylene-isopropyl acetone)
11) 1-Methylamino-4,4-dimethylpentene-1-one-3
12) 1-Methylaminooctene-1-one-3
13) 1-Ethylamino-5-methylhexene-1-one-3
14) 1-Isopropylamino-5-methylhexene-1-one 3
15) 2-Methylaminopentene-2-one-4.

TABLE 5.42

Antiknock Stability of Gasolines after Addition of Salicylalimine Copper Derivatives (According to F.B. Ashbel' et al.)

1 Салициламины, медные производные которых добавлялись в бензины	2 Октановое число при добавлении медных производных, моль/кг					
	0,0025	0,01	0,01	0,016	0,016	0,016
	3 бензина Б-70 (о. ч. = 70,0)		4 Б-70+10% бензола (о. ч. = 71,0)		5 автомобильного бензина+10% бензола (о. ч. = 63,4)	6 смеси гептана, изооктана и бензола (о. ч. = 56,2)
7 Салицилалэтилимин . .	71,8	74,0	74,7	76,4	69,8	65,4
8 Салицилализопропилимин	71,0	75,8	74,7	76,2	69,2	66,2
9 Салицилалбутилимин	71,0	75,8	75,4	—	—	67,0
10 Салицилализоамилимин	70,8	74,4	74,4	76,5	69,2	66,2
11 Салицилалгексилимин	—	—	76,2	—	—	65,6
12 Салицилалгептиламин	—	—	75,9	—	—	—

1) Salicylalimine whose copper derivative was added to the gasoline
2) Octane number on addition of ... mole/kg of copper derivatives
3) B-70 gasoline (70.0-octane)
4) B-70 + 10% benzene (71.0-octane)
5) Automotive gasoline + 10% benzene (63.4-octane)
6) Mixture of heptane, isooctane and benzene (56.2-octane)
7) Salicylalethylimine
8) Salicylalisopropylimine
9) Salicylalbutylamine
10) Salicylalisoamylimine
11) Salicylalhexylimine
12) Salicylalheptylimine.

TABLE 5.43

Receptiveness of Various Fuels to Copper Antiknocks* (According to F.B. Ashbel' et al.)

1 Топливо	2 Октановое число бензинов			
	3 без добавки	4 с медными производными: 5 этиламинометиленацетона	6 метиламинометиленизопропилацетона	7 с ТЭС (в концентрации 0,75 мл/кг)
8 Автомобильные бензины	53,2	—	60,6	72,1
	54,0	—	61,0	65,7
	54,8	64,6	61,2	68,8
	55,1	—	61,3	66,2
9 Прямогонный бензин	56,4	71,4	67,2	74,2
	54,8	—	65,0	73,4
10 Авиационный бензин Б-70	68,0	77,0	77,8	83,5
11 Изооктан-гептановая смесь	40,0	57	53	—
	55	72	67	—
	70	81	79	—

*Content of copper derivative 0.09%.

1) Fuel
2) Gasoline octane number
3) Without additive
4) With copper derivatives
5) Ethylaminomethyleneacetone
6) Methylaminomethyleneisopropylacetone
7) With TEL (concentration 0.75 ml/kg)
8) Automotive gasoline
9) Straight-run gasoline
10) B-70 aviation gasoline
11) Isooctane-heptane mixture.

detonation stability (Tables 5.41-5.43). They come close to the iron-organic antiknocks in effectiveness. However, instability in storage, the accelerating effect on the oxidation of gasolines, and precipitation onto intake-manifold walls have made it impossible to use chelate copper salts as gasoline antiknock additives.

Nonmetallic antiknock additives

One of the most effective antiknocks among the aromatic amines [63-70] is monomethylaniline (N-methylaniline, Table 5.44).

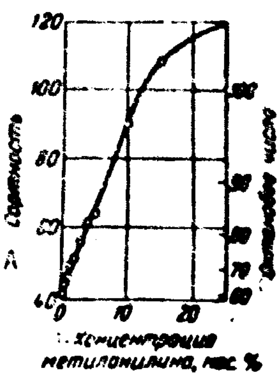


Fig. 5.28. Increase in octane and performance numbers of fuel on addition of monomethylaniline [6]. A) Performance number; B) methylaniline concentration, % by mass; C) octane number.

This compound also meets other requirements made of gasoline additives. Monomethylaniline is more effective when added to low-octane gasolines (Table 5.45). Its introduction improves the antiknock stability of leaded and unleaded gasolines approximately equally (Table 5.46). In the presence of monomethylaniline, the performance numbers of aviation gasolines are increased (Fig. 5.28). Unlike tetraethyllead, the effect of monomethylaniline is not weakened in the presence of sulfur-containing compounds in the gasoline (Table 5.47).

At the end of the Second World War, when the production of TEL was not sufficient to meet the increasing demand for it, up to 2% of xylidine was added to many aviation gasolines in the USA and England [64].

TABLE 5.44

Effectiveness [63] of Aromatic Amines*

A Соединение	B Формула	C Относительная эффективность
D Анилин	$C_6H_5NH_2$	0,8
E о-Толуидин	$CH_3C_6H_4NH_2$	0,9
F 2,6-Диметиланилин	$(CH_3)_2C_6H_3NH_2$	1,1
G о-Этиланилин	$C_2H_5C_6H_4NH_2$	0,5
H 2,6-Диэтиланилин	$(C_2H_5)_2C_6H_3NH_2$	0,3
I N-Метиланилин	$C_6H_5NHCH_3$	1,0
J N-Метил-о-толуидин	$CH_3C_6H_4NHCH_3$	0,6
K N-Метил-2,6-диметиланилин	$(CH_3)_2C_6H_3NHCH_3$	0,2

*The effectiveness of N-methylaniline was taken as 1.0.

A) Compound
B) Formula
C) Relative effectiveness
D) Aniline
E) *o*-Toluidine
F) 2,6-Dimethylaniline
G) *o*-Ethylaniline
H) 2,6-Diethylaniline
I) N-methylaniline
J) N-methyl-*o*-toluidine
K) N-methyl-2,6-dimethylaniline.

TABLE 5.45

Influence of Monomethylaniline on Octane Rating of Paraffin-Base Straight-Run Gasoline [63]

1 Октановое число исходного бензина	2 Октановое число (моторный метод) бензина, содержащего монометиланилин, объемн. %			
	0,5	1,0	1,5	2,0
40,0	43,5	47,0	51,5	54,0
50,0	53,5	57,0	60,0	63,0
60,0	63,5	66,5	69,0	71,0
70,0	73,0	75,5	77,0	73,0
80,0	81,5	82,5	83,0	83,5

1) Octane rating of original gasoline
2) Octane rating (motor) of gasoline containing ... % by volume monomethylaniline.

TABLE 5.46

Influence of Monomethylaniline on Antiknock Stability of Leaded Gasolines [63]

1 Добавка технического монометиланилина, %	2 Октановое число (моторный метод)			
	3 прямогонного бензина	4 бензина, содержащий		7 смесь бензина с бензолом (60 : 40)
		0,02% ТЭС 5	0,06% ТЭС 6	
0	72,0	78,0	83,0	78,5
1	76,5	82,5	87,5	81,5
2	78,5	84,0	89,5	83,0
3	80,0	85,0	90,5	84,0

1) Amount of technical monomethylaniline added, %
2) Motor octane number
3) Straight-run gasoline
4) Gasoline containing
5) 0.02% TEL
6) 0.06% TEL
7) Mixture of gasoline with benzene (60:40).

TABLE 5.47

Influence of Adding 0.1% Ethylmercaptan on Octane Rating of Gasoline Containing TEL and Monomethylaniline [63]

1 Бензин	2 Октановое число (моторный метод)		1 Бензин	2 Октановое число (моторный метод)	
	3 без этилмеркаптана	4 с добавкой 0,1% этилмеркаптана		3 без этилмеркаптана	4 с добавкой 0,1% этилмеркаптана
5 Содержащий ТЭС, %:			6 Содержащий монометиланилин, %:		
0,00	73,0	73,0	0,0	73,0	73,0
0,03	79,5	78,7	0,5	74,8	74,5
0,06	82,0	80,0	1,0	76,0	75,8
			2,0	78,0	77,8

1) Gasoline
2) Motor octane number
3) Without ethylmercaptan
4) With 0.1% ethylmercaptan added
5) Containing TEL, %
6) Containing monomethylaniline, %.

A mixture of aromatic amines with monomethylaniline predominant was at one time manufactured in the USSR under the name Ekstralin and used as an antiknock additive (AUSS 3737-47).

Additives that Improve Fuel Combustion in Diesel and Jet Engines

Alkyl nitrates and peroxide compounds that accelerate the preflame oxidation of the fuel, thus promoting ignition, are used as additives that raise the cetane number of diesel fuels. The ad-

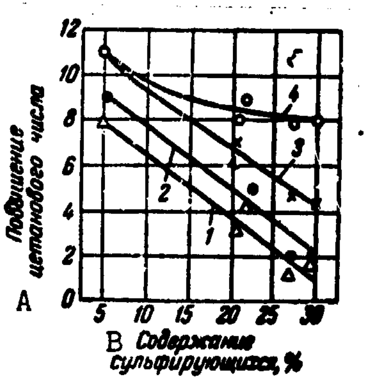


Fig. 5.29. Increase in fuel cetane number on addition of 1% of additives as a function of sulfonating hydrocarbons in the fuel [11]: 1, 4) nitrates; 2, 3) peroxide. A) Cetane number increase; B) content of sulfonating hydrocarbons, %.

ditives are used in low-cetane diesel fuels in amounts of 1.0-2.0% to produce fuels with cetane ratings of 45-50.

The physicochemical properties of the industrial alkyl nitrate additives are listed in Table 5.48. Data on the cetane-number increase obtained when alkyl nitrates and peroxides are added to fuel in amounts of 1.0% by mass are given in Table 5.49.

The effectiveness of the additives depends on fuel chemical composition (Fig. 5.29). The effectiveness of the additives is greater in straight-run fuels than in fuels made from cracking products.

Additives of the alkyl nitrate and peroxide type also improve the combustion of jet fuels. A number of other substances among the esters, sulfur compounds, etc., have been investigated successfully for the same purposes [11].

Combustion catalysts, chiefly organic compounds of metals such as copper, iron, cobalt, chromium, nickel or manganese, can also be used to improve combustion [74].

TABLE 5.48

Physicochemical Properties of Alkyl Nitrates [71, 72]

1 Присадка	2 Плотность ρ_4^{20}	3 Показатель преломления n_D^{20}	4 Температура, °C		7 Молекулярный вес
			5 кипения	6 вспышки	
8 Амилнитрат	0,998	1,413	152	42	133
9 Изопропилнитрат	1,02	—	98	—	105

1) Additive
2) Density
3) Refractive index
4) Temperatures, °C
5) Boiling point
6) Flash point
7) Molecular weight
8) Amyl nitrate
9) Isopropyl nitrate.

TABLE 5.49

Increase in Fuel Cetane Number on Addition of Alkyl Nitrates and Peroxides [73]

1 Присадка	2 Цетановое число топлива без присадки	3 Повышение цетанового числа топлива
4 Изопропилнитрат	44,0	17,0
5 Бутилнитрат	44,0	19,0
6 Амилнитрат	44,0	23,0
7 Перекись бутила	39,1	20,2
8 Перекись гептила	49,3	16,1

1) Additive
2) Cetane number of fuel without additive
3) Increase in fuel cetane number
4) Isopropyl nitrate
5) Butyl nitrate
6) Amyl nitrate
7) Butyl peroxide
8) Heptyl peroxide.

3. ADDITIVES THAT IMPROVE THE STABILITY OF FUELS IN STORAGE, SHIPMENT AND USE AT THE ENGINES

Additives of this group include substances that tend to retard the oxidation processes of fuels. Oxidation of fuels is detrimental to their quality. The additives also moderate the detrimental effects of the oxidation products formed.

Antioxidation Additives (Antioxidants)

Antioxidants are added to fuels in quantities ranging from thousandths to tenths of a per cent, depending on the type of antioxidant and the fuel. Soviet and foreign commercial antioxidants are characterized in Table 5.50.

TABLE 5.50

Commercial Antioxidants Used to Stabilize Various Types of Fuels [14, 75]

1 Присадка	2 Применяемые концентрации, мас. %	3 Физические свойства: 4 внешний вид	5 плотность d_4^{20}	6 Температура, °С: 7 кипения	8 плавления	9 вспышки	10 молекулярный вес активного компонента	11 Область применения
12 Ионол, топанол О, Дюпон № 29 (2,6-ди-*трет*-бутил-4-метил-*п*-фенол)	0,004—0,03	13 Кристаллы белого и светло-желтого цвета	1,04	260	69	127	220,4	14 Автомобильные и авиационные бензины, реактивные топлива
15 Топанол А (2,4-диметил-6-*трет*-бутил-*п*-фенол)	0,004—0,03	16 Бледно-желтая жидкость	0,961	246—262	—	110	178,2	17 То же
18 *п*-Оксидифениламин	0,004—0,008	Светло-серый порошок	0,961	330	66—74	—	185,2	20 Авиационные и автомобильные бензины
21 Дюпон № 5, тенамен-1 UOP № 4* (N, *н*-бутил-*п*-аминофенол)	0,002—0,005	19 Жидкость 22	0,90	—	—30	16	165,2	Главным образом бензины; 23 авиационные топлива
24 UOP № 5, Дюпон № 22, тенамен-2, топанол М (N, N′-ди-*втор*-бутил-*п*-фенилендиамин)	0,002—0,006	25 Красная жидкость	0,95	295—300	15	146	220,3	26 Рекомендован для авиационных керосинов. Главным образом топлива, содержащие продукты крекинга; для облагораживания сернистых бензинов
27 ФЧ-16 (фенолы из подсмольных вод угольной смолы)	0,05—0,1	28 Темно-коричневая жидкость	1,15	29 до 220° С 40% до 270° С 90%	—	—	—	30 Автомобильные бензины, тракторные керосины 31 Рекомендован для авиационных керосинов
32 ФЧ-4 (фенолы из фракции угольной смолы)	0,05—0,1	17 То же	1,07		—	—	150	17 То же
33 Древесно-смольный антиокислитель сорта «Б», UOP № 1* (фенолы из древесной смолы)	0,05—0,1	»	1	230—310	—	—	—	Автомобильные бензины, 30 тракторные керосины
34 Пиронизат	35	Коричневая жидкость	1,06	до 243° С 52%	—	—	—	17 То же

*Contains 50% of absolute methanol or isopropanol as a solvent.

1) Additive
2) Concentration used, % by mass
3) Physical properties
4) External appearance
5) Density
6) Temperatures, °C
7) Boiling point
8) Melting point
9) Flash point
10) Molecular weight of active component
11) Field of application
12) Ionol, Topanol O, Diopon No. 29 (2,6-di-*tert*-butyl-4-methyl-p-phenol)
13) White and light yellow crystals
14) Automotive and aviation gasolines, jet fuels
15) Topanol A (2,4-dimethyl-6-*tert*-butyl-*p*-phenol)
16) Pale yellow liquid
17) Same
18) p-hydroxydiphenylamine
19) Light gray powder
20) Aviation and automotive gasolines
21) Diopon No. 5, Tenamen-1, UOP No. 4* (N,*n*-butyl-*p*-aminophenol)
22) Liquid
23) Chiefly gasolines; aviation fuels
24) UOP No. 5, Diopon No. 22, Tenamen-2, Topanol M (N,N'-di-*sec*-butyl-*p*-phenylenediamine)

25) Red liquid
26) Recommended for aviation kerosenes. Principally fuels containing cracking products; to improve sulfur-containing gasolines
27) FCh-16 (phenols from coal tar water)
28) Dark brown liquid
29) Below
30) Automotive gasolines, tractor kerosenes
31) Recommended for aviation kerosenes
32) FCh-4 (phenols from coal-tar fractions)
33) Wood-tar antioxidant, grade "B," UOP No. 1" (phenols from wood tar)
34) Pyrolyzate
35) Brown liquid.

The most widely used among domestic antioxidants is *p*-hydroxydiphenylamine (phenyl-*p*-aminophenol), which is effective in all types of fuels: it stabilizes the decay of the tetraethyllead in leaded aviation gasolines and the oxidation of unsaturated hydrocarbons in automotive gasolines and aviation kerosenes. A disadvantage is its poor solubility in fuels, which makes it necessary to introduce it into the fuel in the form of a solution in aromatic hydrocarbons or in highly aromaticized gasoline. The alkyl phenol antioxidant Ionol – 2,6-di-*tert*-butyl-4-methylphenol[1] – dissolves without limit in fuels and is completely insoluble in water.

TABLE 5.51

Technical Specifications for *p*-Dihydroxydiphenylamine (TU U-3639-52)

1 Показатели	2 Нормы
3 Внешний вид	4 Твердая сплавленная масса от светло-серого до серого цвета
5 Температура плавления, °C	69—74
6 Реакция водной вытяжки	7 Нейтральная
8 Примеси, нерастворимые в бензоле (при содержании 4 г продукта в 100 мл бензола), %, не более	0,2
9 Зольность, %, не более	0,05
10 Растворимость в бензине Б-70	11 При добавлении к 100 мл бензина 0,75 мл раствора п-оксидифениламина в бензоле (4 г на 100 мл) раствор должен быть прозрачен

1) Index
2) Norms
3) External appearance
4) Solid fused mass from light gray to gray in color
5) Melting point, °C
6) Reaction of water extract
7) Neutral
8) Impurities insoluble in benzene (for content of 4 g of the product in 100 ml of benzene), %, no more than

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9) Ash, %, not above
10) Solubility in B-70 gasoline
11) On addition of 0.75 ml of solution of *p*-hydroxydiphenylamine in benzene (4 g to 100 ml) to 100 ml of gasoline, the solution must be transparent.

TABLE 5.52

Technical Specifications for FCh-16 Antioxidant (VTU MNP 590-56) and Wood-Tar Straight-Run Antioxidant (AUSS 3181-63)

1 Показатели	2 ФЧ-16	3 Древесно-смоляной антиокислитель
4 Внешний вид	5 Однородная свободная от механических примесей маслянистая жидкость коричневого или темно-коричневого цвета	6 Темная маслянистая жидкость
7 Плотность ρ_4^{20}, не ниже	1,00	1,060—1,100
8 Содержание, %:		
9 бутилацетата, не более	4	—
10 фенолов, не менее	85	60
11 примесей, нерастворимых в топливе	12 Отсутствие	—
13 Кислотное число, мг KOH на 1 г, не более	20	30
14 Прирост содержания смол в 100 мл бензина при добавлении 50 мг антиокислителя, мг, не более	1,5	1,5
15 Фракционный состав:		
16 до 220° С перегоняется, включая воду*, объемн. %, не более	48	—
16 до 240° С перегоняется, включая воду, объемн. %, не более	56—66	25
16 до 260° С перегоняется, включая воду, объемн. %, не более	70—75	55
16 до 270° С перегоняется, включая воду, объемн. %, не менее	85	90**
17 Вода, %, не более	6	6

*Effective as of 1 January 1965.
**Below 310°C.

1) Index
2) FCh-16
3) Wood-tar antioxidant
4) External appearance
5) Homogeneous brown or dark brown oily liquid, free of mechanical impurities
6) Dark oily liquid
7) Density ρ_4^{20}, not below
8) Contents, %
9) Butyl acetate, not above
10) Phenols, not below
11) Impurities insoluble in fuel
12) None
13) Acid number, mg of KOH to 1 g, not above
14) Increase in tar content in 100 ml of gasoline on addition of 50 mg of antioxidant, mg, not above
15) Fractional composition
16) Distill below ...°C, including water,* % by volume, not above
17) Water, % not above.

TABLE 5.53

Physicochemical Properties of FCh-4 Antioxidant (TU MNP 285-49)

1 Показатели	2 Нормы
3 Плотность ρ_4^{20}	1,073
4 Молекулярный вес . . .	150
5 Гидроксильное число . .	12,0
6 Нейтральные соединения, мас. %	3,8
7 Зольность, %	0,002
8 Вода по Дину и Старку, %	Следы

1) Index
2) Norm
3) Density
4) Molecular weight
5) Hydroxyl number
6) Neutral compounds, % by mass
7) Ash
8) Dean-Stark water.

TABLE 5.54

Physicochemical Properties of Pyrolyzate

1 Показатели	2 Нормы
3 Плотность ρ_4^{20}	1,06
4 Содержание фракций, выкипающих до 240° С, %	52
5 Кислотное число, мг КОН на 1 г топлива	80
6 Содержание о-диоксибензолов, %	11

1) Index
2) Norm
3) Density
4) Content of fractions boiling over below 240°C, %
5) Acid number, mg of KOH to 1 g of fuel
6) Content of *o*-dihydroxybenzenes, %.

TABLE 5.55

Effectiveness of Antioxidants in Automotive Gasoline*

1 Антиокислитель	2 Смолы фактические (в мг на 100 мл) после окисления при 110° С в присутствии меди		
	3 2 ч	4 ч	8 ч
4 Бензин каталитического крекинга без антиокислителя	13	25	30
5 Древесносмольный сорта Б	11	13	20
6 ФЧ-16	3	1	4
7 Пиролизат	5	3	4

*Concentration 0.05% by mass.

1) Antioxidant
2) Existent gums (in mg to 100 ml) after oxidation at 110°C in the presence of copper
3) 2 hours
4) Catalytic cracking gasoline without antioxidant
5) Grade B wood-tar antioxidant
6) FCh-16
7) Pyrolyzate.

TABLE 5.56

Influence of Antioxidants on Gum Formation in Automotive Gasolines

1 Антиокислители, добавляемые к бензинам	2 Концентрация антиокислителя, мас. %	3 Условия испытания	4 Время, необходимое для образования 20 мг смол на 100 мл горючего, сутки
5 *Бензин термического крекинга [63]:*			
6 без антиокислителя	—	7 Хранение при температуре 40° C	10
древесносмольный сорта Б	0,065		54
8 ФЧ-16	0,065		120
9 То же	0,033		33
10 *п*-оксидифениламин	0,0065		26
11 *Бензин А-72 [61]:*			
6 без антиокислителя	—	12 Хранение при 45—50° C в присутствии медной пластинки (3 *см²/л*)	22
древесносмольный сорта Б	0,065		110
8 ФЧ-16	0,03		15 Более 170
10 *п*-оксидифениламин	0,008		» 170
13 *Бензин А-72 [65]:*			
6 без антиокислителя	—	14 Окисление при 110° C в присутствии катализатора меди	3*
древесносмольный сорта Б	0,05		6*
8 ФЧ-16	0,05		15 Более 6*
16 улучшенный древесносмольный антиокислитель (пиролизат)	0,05		» 6*

1) Antioxidant added to gasolines
2) Antioxidant concentration, % by mass
3) Test conditions
4) Time necessary for formation of 20 mg of gums to 100 ml of fuel, days
5) Catalytic cracking gasoline [63]
6) Without antioxidant
7) Storage at 40°C
8) FCh-16
9) Same
10) *p*-hydroxydiphenylamine
11) A-72 gasoline [61]
12) Storage at 45-50°C in presence of copper plate (3 cm²/liter)
13) A-72 gasoline [65]
14) Oxidation at 110°C in presence of copper catalyst
15) More than
16) Improved wood-tar antioxidant (pyrolyzate).

TABLE 5.57

Effectiveness of Antioxidant in Diesel Fuel Containing Cracking Components [78]

1 Добавляемые антиокислители	2 Концентрация антиокислителя, мас. %	3 Смолы *, мг на 100 мл	
		4 топливо с 30% крекинг-компонента	5 топливо с 20% компонента каталитического крекинга
6 Топливо без антиокислителя	—	54	42
7 Пиролизат	0,1	37	27
8 ФЧ-16	0,1	33	23
9 Ионол	0,1	33	31
10 n-Оксидифениламин	0,015	38	24

*Oxidation for 2 hr at 120°C in the presence of copper.

1) Antioxidant added
2) Antioxidant concentration, % by mass
3) Gums,* mg to 100 ml
4) Fuel with 30% cracking component
5) Fuel with 20% catalytic cracking component
6) Fuel without antioxidant
7) Pyrolyzate
8) FCh-16
9) Ionol
10) p-hydroxydiphenylamine.

TAPLE 5.58

Chemical Stability of Leaded Aviation Gasoline Components* [6] [79]

1 Бензины	2 Период стабильности по ГОСТ 6667—56 (при 110° С), ч	
	3 без антиокислителя	4 с 0,004% мас. % n-оксидифениламина
5 Бакинские прямой гонки:		
6 из сураханской нефти	~1	20
7 из балаханской нефти	~1	15
8 из биби-эйбатской нефти	~1	14
9 Каталитического крекинга (алканкомпоненты):		
10 из гурьевской нефти	1	28
11 из орской нефти	1	32
12 Технические алкилбензолы:		
13 образец 1	<0.5	8
образец 2	<0.5	1
14 Технические алкилаты:		
10 из гурьевской нефти	1.5	18
11 из орской нефти	1.5	21

*TEL content 0.33% by mass.

1) Gasoline
2) Period of stability according to AUSS 6667-56 (at 110°C), hr
3) Without antioxidant
4) With 0.004% by mass of p-hydroxydiphenylamine
5) Baku straight-run

6) From Surakhany petroleum
7) From Balakhany petroleum
8) From Bibi-Eybat petroleum
9) Catalytic cracking (aviation components)
10) From Gur'yev petroleum
11) From Orsk petroleum
12) Technical alkyl benzenes
13) Specimen ...
14) Technical alkylates.

TABLE 5.59

Effectiveness of *p*-Hydroxydiphenylamine in Retarding Decomposition of Tetraethyllead in Aviation Gasolines [72]

1 Показатели	2 Бензин без антиокислителя	3 Бензин с п-оксидифениламином (0,004 мас. %)
4 Период стабильности по ГОСТ 6667—56 (при 110° С), ч	<1	>8
5 Продолжительность хранения на складах в условиях южной зоны до образования свинцовистого осадка . . .	14	36

1) Index
2) Gasoline without antioxidant
3) Gasoline with *p*-hydroxydiphenylamine (0.004% by mass)
4) Stability period according to AUSS 6667-56 (at 110°C), h
5) Permissible dump storage time under conditions of southern zone to formation of lead-containing precipitate.

TABLE 5.60

Effectiveness of Antioxidants in Aviation Kerosene Containing Cracking Components [80]

1 Антиокислитель	2 Концентрация антиокислителя, мас. %	3 Время окисления при 110° С до образования 15 мг смол на 100 мл топлива, мин	4 Количество смол, мг на 100 мл за 10 ч при 110° С
5 Древесносмоляный сорта Б . .	0,05	450	26
6 п-Оксидифениламин	0,01	550	21
7 Ионол	0,1	595	10
8 ФЧ-4	0,05	585	16

1) Antioxidant
2) Antioxident concentration, % by mass
3) Time of oxidation at 110°C to formation of 15 mg of gums per 100 ml of fuel, min
4) Amount of gums, mg to 100 ml after 10 h at 110°C
5) Grade B wood-tar antioxidant
6) p-Hydroxydiphenylamine
7) Ionol
8) FCh-4.

Phenolic antioxidants from coal and wood tars, even the most effective ones, are useful only to stabilize fuels containing unsaturated hydrocarbons. Grade B wood-tar antioxidant is inferior in effectiveness to other wood-tar antioxidants (grade "A,"[2] "inhibitor preparation,"[2] pyrolyzate) and to phenolic antioxidants obtained from coal – FCh-16, FCh-4. It is obtained from the tars of destructive distillation of various species of wood [76] (preferably birch and beechwoods); it represents the 230-310°C fraction of these tars.

Pyrolyzate is obtained by pyrolysis of wood-tar oils. In this process, some of the less active compounds in the wood tar are converted to more active antioxidants [78].

FCh-4 antioxidant is obtained from the kerosene fraction of semicoking tar from Cheremkhovo coals (TU MNP 285-49), and FCh-16 from the semicoking-tar water of Cheremkhovo coals by extraction of the phenols with butyl acetate, which is then boiled off. The content of phenols in the antioxidant is ~85% [77].

Tables 5.51-5.54 present the technical specifications for the basic domestic commercial antioxidants, and Tables 5.55-5.60 data characterizing their effectiveness when added to certain petroleum products.

Metal Deactivators

Metal deactivators are added to fuels to suppress the catalytic action of active metals (for example, copper), which accelerate hydrocarbon oxidation.

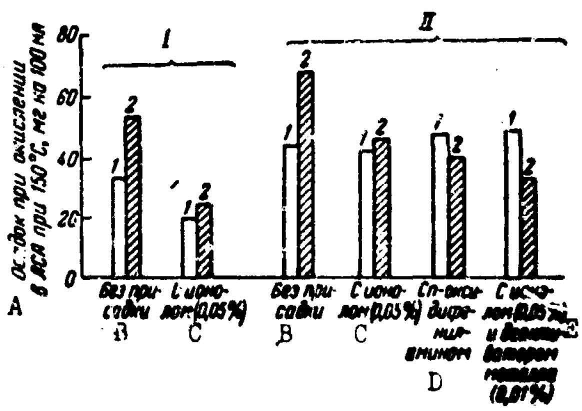

Fig. 5.30. Influence of antioxidants on retention of thermal stability of aviation fuels [21] (storage for 4 months at 50°C): I) T-5 fuel; II) T-1 fuel; 1) before storage; 2) after storage. A) Sediment in oxidation in LSA at 150°C, mg per 100 ml; B) without additive; C) with Ionol (0.05%); D) with p-hydroxydiphenylamine; E) with Ionol (0.05%) and metal deactivator (0.01%).

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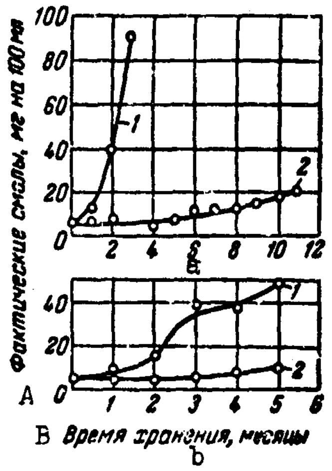


Fig. 5.31. Influence of metal deactivator on storage stability of gasolines [13]: I) southern climatic zone; II) middle climatic zone; 1) gasoline with antioxidant only; 2) gasoline with antioxidant and metal deactivator. A) Existent gums, mg to 100 ml; B) storage time, months.

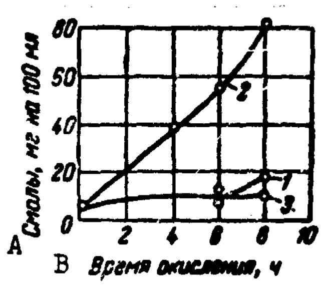
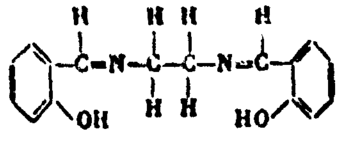
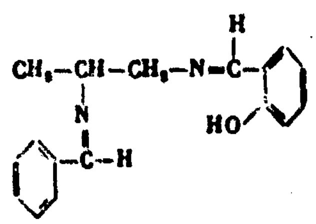
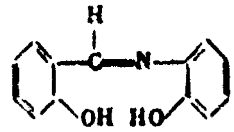


Fig. 5.32. Stabilization of aviation kerosenes by metal deactivators [15] (oxidation at 110°C): 1) in the absence of copper; 2) in the presence of copper; 3) in presence of copper and metal deactivator. A) Gums, mg to 100 ml; B) oxidation time, h.

TABLE 5.61

Physicochemical Properties of Metal Deactivators

1 Дезактиваторы	2 Формула	3 Внешний вид	Температура плавления или застывания, °C 4	Плотность ρ_4^{20}, г/см³ 5	6 Растворимость
7 Дисалицилиденэтилендиамин (ДМС)		8 Лимонно-желтые чешуйчатые кристаллы	123—126	—	9 В топливе, бензоле, спирте; в воде не растворим
10 1,2-Дисалицилиденпропилендиамин (ДМД, Тенатен-60)		11 Темно-янтарная жидкость	—18	1,08	12 То же
13 Салицилиден-о-аминофенол		14 Оранжевые блестящие кристаллы	175	—	15 В топливе трудно, хорошо в ацетоне

1) Deactivator
2) Formula
3) External appearance
4) Melting or pour point, °C
5) Density ρ_4^{20}, g/cm³
6) Solubility
7) Disalicylideneethylenediamine (ДМС)
8) Lemon-yellow plates
9) In fuel, benzene, alcohol; insoluble in water
10) 1,2-Disalicylidenepropylenediamine (ДМД, Tenaten-60)
11) Dark amber liquid
12) Same
13) Salicylidene-*o*-aminophenol
14) Lustrous orange crystals
15) Difficult in fuel, good in acetone.

TABLE 5.62

Effectiveness of Metal Deactivators in Cracking Kerosene [75]

1 Антиокислитель	2 Концентрация антиокислителя, мас. %	3 Смолы после ускоренного окисления,* мг на 100 мл			
		4 без металла	5 в присутствии меди	6 с медью и добавлением деактиватора металла ** I	II
7 п-Оксидифениламин	0,02	24	129	28	18
8 Ионол	0,2	24	68	30	26
9 ФЧ-16	0,1	21	32	19	—
ФЧ-4	0,1	24	64	19	28
10 Древесносмольный сорт Б	0,1	11	212	50	—

*Oxidation for 4 h at 100°C.
**I is salicylidene-*o*-aminophenol (0.013%); II is disalicylideneethylenediamine (0.02%).

1) Antioxidant
2) Antioxidant concentration, % by mass
3) Gums after accelerated oxidation,* mg to 100 ml
4) Without metal
5) In presence of copper
6) With copper and metal deactivator additive**
7) *p*-Hydroxydiphenylamine
8) Ionol
9) FCh-16
10) Grade B wood-tar antioxidant.

TABLE 5.63

Stabilization of Tetraethyllead Decomposition by Metal Deactivators [98]

1 Добавляемые деактиваторы	2 Концентрация деактиватора мг/на 100 мл	3 Содержание этиловой жидкости Р-9, мл/кг		6 Осадок после ускоренного окисления
		4 до окисления	5 после ускоренного окисления	
7 Бензин авиационный без присадок	—	4,1	2,97	8 Обильный белый
9 Салицилиден-*о*-аминофенол	10	4,1	4,05	10 Отсутствует
11 Дисалицилиденэтилендиамин	15	4,1	4,07	»

1) Deactivators added
2) Deactivator concentration, mg/100 ml
3) R-9 ethyl fluid content, ml/kg
4) Before oxidation
5) After accelerated oxidation
6) Sediment after accelerated oxidation
7) Aviation gasoline without additive
8) Abundant, white
9) Salicylidene-*o*-aminophenol
10) None
11) Disalicylideneethylenediamine.

TABLE 5.64

Effectiveness of Metal Deactivator in Sulfur-Containing Diesel Fuel with Catalytic Cracking Component

1 Образцы	2 Концентрация присадки, мас. %	3 Смолы *, мг на 100 мл
4 Топливо		
5 без присадок	—	42
6 с пиролизатом	0,1	16
7 с деактиватором металла	0,01	
8 с ФЧ-4	0,1	18
7 с деактиватором металла	0,01	

*Oxidation for 2 h at 120°C in presence of copper.

1) Specimen
2) Additive concentration, % by mass
3) Gums,* mg to 100 ml
4) Fuel
5) Without additives
6) With pyrolyzate
7) With metal deactivator
8) With FCh-4.

In themselves, metal deactivators have no significant antioxidant effect and, as a rule, are not used without antioxidants. Their optimum concentrations are 5-10 times smaller than those of antioxidants. The metal deactivator forms, with the metal ions, complexes of a certain structure, in which the metal is in an inactive state. Hence only compounds capable of forming complexes with "claw-like" structure (or "chelates") can be used as such additives.

Salicylidenes — condensation products of salicylaldehyde with amines or aminophenols — have come into use as commercial metal deactivators. Salicylidene-*o*-aminophenol, disalicylideneethylenediamine, and disalicylidenepropylenediamine have proven most effective. In ready-to-use form, the additives are 20-50% solutions of the salicylidene in toluene or xylene as a solvent.

The properties of metal deactivators in pure form are given in Table 5.61. Their addition to all types of fuels — gasolines, aviation and diesel fuels — is recommended. Tables 5.62-5.64 and Figs. 5.30-5.32 show the effectiveness of metal deactivators in various fuels.

Metal deactivators are also effective in stabilizing the decomposition of TEL even when antioxidants are not present.

Dispersing Stabilizers that Prevent Formation of Insoluble Sediment in Fuels

Dispersing-agent stabilizers are added to fuels that have a tendency to form insoluble products on oxidation (for example, those containing sulfur, diesel fuels with cracking components, distillate boiler fuels), with the purpose of protecting the fuels from oxidation and dispersing insoluble products that have formed in them. These functions may be performed in the additive by two or more different chemical compounds or by a single compound exhibiting both types of properties.

As a rule, dispersing agents are surface-active compounds. They prevent the coagulation and adhesion of fuel-insoluble particles into large aggregates that are capable of settling. The action of the dispersing agents is similar to that of peptizers in colloidal systems.

Formation of insoluble oxidation products is observed in medium distillate fuels, including the kerosene and gas-oil fractions, chiefly as a result of nonhydrocarbon fuel components: sulfur, nitrogen, and oxygen compounds. This process takes place slowly in most fuels at normal storage temperatures. Fuels containing active sulfur compounds and considerable quantities of cracking products are an exception. At elevated temperatures, which may arise in the fuel systems of "hot" modern engines, the oxidation processes of unsaturated fuel components are accelerated and measures against the formation of fuel-insoluble products become an important use problem.

Dispersing agents are classified as ash-containing and ash-free depending on their chemical nature. The former include metals

TABLE 5.65

Physicochemical Properties of Dispersing Fuel Additives

1 Показатели	2 Сульфонаты (зольные)	3 Полярные сополимеры (беззольные)	
		I *	II **
4 Плотность, ρ_4^{20}	—	0,902	0,8740
5 Вязкость кинематическая при 100° С, *сст*	18—20	65	20
6 Коэффициент преломления n_D^{20}	—	—	1,4550
7 Температура, °С:			
8 вспышки	180	41	—
9 застывания	—	—29	—
10 Кислотное число, *мг* КОН на 1 *г*	—	—	0,2
11 Растворимость в воде, мас. %	—	12 Менее	—
13 Зольность, %, не менее	3,6	14 Отсутствие	
15 Щелочность эквивалентная, *мг* КОН на 1 *г*	5	13,8	—
16 Механические примеси, %, не более	0,1	14—	—
17 Вода, %		Отсутствие	

*The commercial American additive "DuPont FOA-2." A copolymer of dodecyl methacrylate and diethylaminoethyl methacrylate.
**Experimental specimen.

1) Index
2) Sulfonates (ash)
3) Polar copolymers (ash-free)
4) Density
5) Kinematic viscosity at 100°C, cSt
6) Refractive index
7) Temperatures, °C
8) Flash point
9) Pour point
10) Acid number, mg of KOH to 1 g
11) Water solubility, % by mass
12) Less
13) Ash, %, not below
14) None
15) Alkali equivalent, mg of KOH to 1 g
16) Mechanical impurities, %, no more than
17) Water, %.

TABLE 5.66

Technical Specifications for VNII NP-102 Boiler Fuel Additive (from VTU NP 39-59)

1 Показатели	2 Нормы	3 Методы испытаний
4 Плотность ρ_4^{20}, не менее	0,980	5 ГОСТ 3900—47
6 Количество нафталина, %, не более	5,0	По п. 4 настоящих техни-7 ческих условий
8 Фракционный состав:		
9 начало кипения, °С, не ниже	180	ГОСТ 2177—59
10 до 305° С перегоняется, %, не менее	78	11 Остаток после отгона 95% должен быть подвижным при температуре 20° С
12 до 350° С перегоняется, %, не менее	95	
13 Температура, °С:		
14 вспышки (в открытом тигле), не ниже	55	ГОСТ 4333—48
15 застывания, не выше	—10	16 ГОСТ 1533—42; без предварительного и последующего нагрева до 50° С

TABLE 5.66 (continued)

1 Показатели	2 Нормы	3 Методы испытаний
17 Иодное число, г I на 100 г присадки, не более	18	ГОСТ 2070—55
18 Коксуемость, %, не более	0,75	ГОСТ 5937—51
19 Сульфирующие вещества, %, не менее	98	ГОСТ 2706—57, п. XI 20
21 Вода, %, не более	2,0	ГОСТ 2477—44

1) Index
2) Norm
3) Test method
4) Density ρ_4^{20}, not below
5) AUSS 3900-47
6) Amount of naphthalene, %, not above
7) Section 4 of these technical specifications
8) Fractional composition
9) Start of boiling, °C, not below
10) Distilled below 305°C, %, not below
11) Residue after 95% distillation should be mobile at 20°C
12) Distilled over below 350°C, %, no less than
13) Temperatures, °C
14) Flash point (open crucible), not below
15) Pour point, not above
16) AUSS 1533-42; without preliminary or subsequent heating to 50°C
17) Iodine number, g of I to 100 g of additive, not above
18) Coking capacity, %, not above
19) Sulfonating substances, %, not below
20) ..., Section XI
21) Water, %, not above.

TABLE 5.67

Influence of Dispersing Stabilizers on Formation of Insoluble Residues in Fuel during Storage [81]

1 Присадка	2 Нерастворимый осадок (в мг на 100 мл) после хранения при 43° С	
	3 6 недель	4 18 недель
5 Без присадки	5,8	15,0
6 Алкиламин	2,4	9,0
7 Сульфонат металла	0,6	7,8
8 Полярный полимер	1,1	5,3

1) Additive
2) Insoluble residue (in mg to 100 ml) after storage at 43°C
3) 6 weeks
4) 18 months
5) Without additive
6) Alkylamine
7) Metal sulfonate
8) Polar polymer.

TABLE 5.68

Influence of Additives on Fuel Thermal Stability [6]

A Топливо	B Присадка	C Концентрация присадки, мас. %	D Условия окисления	E Осадок, мг на 100 мл
F Смесь топлива Г-2 с 30% крекинг-компонента	G Без присадки	—	I 120° C, 6 ч, с пластинкой из бронзы ВБ-24	9
	H Алифатические амины $C_{10}—C_{40}$	0,05		1
J Топливо ТС-1, содержащее 0,045% меркаптановой серы	G Без присадки	—	K То же	20
	H Алифатические амины $C_{10}—C_{40}$	0,05	»	3
L Топливо Т-1	G Без присадки	—	N 150° C, 4 ч, с медной пластинкой	19
	M Полярный полимер FOA-2	0,05		2
O Топливо ТС-1	G Без присадки	—	K То же	8
	M Полярный полимер FOA-2	0,05	»	2

A) Fuel
B) Additive
C) Additive concentration, % by mass
D) Oxidation conditions
E) Sediment, mg to 100 ml
F) Mixture of fuel T-2 with 30% cracking component
G) Without additives
H) C_{10}-C_{40} aliphatic amines
I) 120°C, 6 hr, with VB-24 bronze plate
J) Fuel TS-1 containing 0.045% mercaptan sulfur
K) Same
L) Fuel T-1
M) Polar polymer FOA-2
N) 150°C, 4 hr, with copper plate
O) Fuel TS-1.

as salts of petroleum sulfo acids (calcium or barium sulfonates) or of naphthenic acids. The ash-free dispersing additives include aliphatic alkylamines and the so-called polar polymers, which are products of copolymerization of two (or three) monomers of which one carries the active properties of the additive and contains a polar group (nitrogen base), while another is a nonpolar compound and forms the oleophilic part of the additive, which ensures that it will be soluble in the fuel. The third monomer, if there is one, performs no additional functions, but serves only to lengthen the copolymer chain.

The physicochemical properties of various dispersing stabilizers are listed in Tables 5.65 and 5.66. Their effectiveness is characterized by the data given in Tables 5.67 and 5.68.

Figures 5.33 and 5.34 and Table 5.69 show the influence of adding ash- and ash-free-type dispersing agents on the high-temperature filterability of fuels.

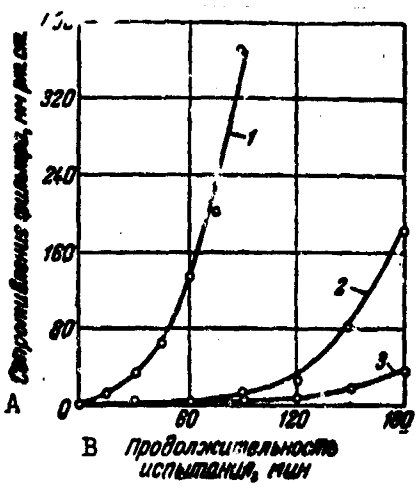


Fig. 5.33. Improvement of diesel-fuel filterability at elevated temperatures from the use of dispersing stabilizers: 1) fuel without additive; 2) with amine-type additive, 0.05%; 3) with polar-polymer-type additive, 0.05%. A) Filter resistance, mm Hg; B) test time, min.

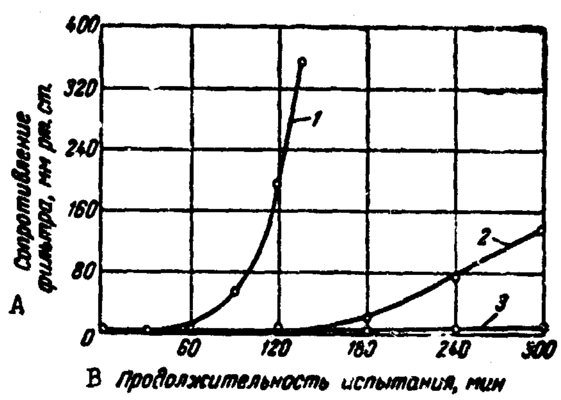


Fig. 5.34. Improvement of high-temperature filterability of aviation kerosenes from the use of dispersing stabilizers: 1) fuel without additive; 2) with sulfonate additive; 3) with polar-polymer additive. A) Filter resistance, mm Hg; B) test time, min.

In residual boiler fuels, dispersing stabilizers prevent formation of sludges, ensure compatibility of different fuels and inhibit the settling of asphalt-tar substances. Use of these additives makes it possible to reduce the amount of labor and money spent on removing asphalt-tar sediment from storage tanks. This method of cleaning tanks is about 30 times more economical than the most commonly used mechanical procedure [82].

The additive VNII NP-102, which is a fraction of naphthalene homologues, basically disubstituted naphthalenes (see Table 5.66) is an effective commercial additive for residual fuels. VNII NP-103, a modification of this additive, contains, in addition to the naphthalene homologues, small quantities of various elements: 0.26% barium, 0.12% phosphorus and 0.42% copper. The barium and phosphorus are introduced in the form of a barium alkyldithiophosphate or a barium phenolate and an alkyldithiophosphate, and have the function of enhancing the dispersing and anticorrosion properties of the additive. Copper is introduced in the form of the naphthenate and serves to improve combustion of the fuel.

TABLE 5.69

Influence of Dispersing Stabilizers on Thermal Stability of Fuels [77]

1 Топливо	2 Температура испытания, °C	3 Термическая стабильность (время до засорения фильтра), мин	
		4 без присадки	5 с присадкой типа сополимеров
6 Топливо Т-5	180	90	>300
7 То же	200	240	>300
8 Дизельное сернистое	160	10	>300

1) Fuel
2) Test temperature, °C
3) Thermal stability (time to clogging of filter), min
4) Without additive
5) With copolymer-type additive
6) T-5 fuel
7) Same
8) Sulfur-containing diesel fuel.

Dispersing additives of various types can be used together – for example, polar copolymers mixed with primary alkylamines [83]. In this case we observe a synergistic effect. The recommended ratio of amine to copolymer in such additives ranges from 3:1 to 8:1 (on the active polymer component). The concentration of the combined additive in the fuel ranges from 0.001 to 0.045% by mass.

4. ADDITIVES THAT REDUCE THE HARMFUL EFFECT OF FUELS ON APPARATUS AND MECHANISMS

Additives of this group include substances that are capable of mitigating the harmful effects that the fuel may have on apparatus and mechanisms during use. They are the corrosion inhibitors, additives that reduce wear of fuel-system rubbing parts (antiwear additives), those that reduce varnish and deposit formation and wear in the piston-cylinder group of the engine, and additives that reduce corrosion of gas turbines by the combustion products of residual fuels.

Anticorrosion Additives

Corrosion inhibitors (or anticorrosion additives) can be used effectively in fuels of all types. Metal corrosion is caused by the products of fuel oxidation or by active sulfur compounds. Hence the fuels most aggressive toward metals are those containing substantial quantities of unstable hydrocarbons or active sulfur compounds (chiefly mercaptans). Rapid corrosion is observed in leaded gasolines as a result of their content of halide scavengers. Corrosion is intensified when water is present in the fuel – either dissolved or as a separate phase – since the rate of electrochemical corrosion then rises sharply.

TABLE 5.70

Technical Specifications for KSK and ASK Sulfonates (from Interdepartmental TU)

1 Показатели	2 Сульфонат кальция КСК	3 Сульфонат аммония АСК
4 Вязкость кинематическая при 100° С, *сст*	18—20	15—25
5 Температура вспышки (в открытом тигле), °С не ниже	180	1[illegible]
6 Зольность, %, не менее	3,6	—
7 Щелочность по синему бромфенолу, *мг* КОН на 1 *г*, не менее	5,0	1,0
8 Механические примеси, %, не более	0,1	0,1
9 Вода	10 Отсутствие	

1) Index
2) KSK calcium sulfonate
3) ASK ammonium sulfonate
4) Kinematic viscosity at 100°C, cSt
5) Flash point (open crucible), °C, not below
6) Ash, %, not below
7) Bromphenol blue alkalinity, mg of KOH to 1 g, not below
8) Mechanical impurities, %, not above
9) Water 10) None.

TABLE 5.71

Physicochemical Properties of NG-203 Additive

1 Показатели	2 Марка		
	А	3 Б	4 В
5 Содержание, %, на смазку:			
6 100%-ного сульфоната кальция	12—14	7—10	7—10
7 окисленного петролатума	10—12	6—8	6—8
8 Вязкость кинематическая (в *сст*) при:			
50° С	—	—	25—33
100° С	25—50	10—15	—
9 Температура вспышки (в открытом тигле), °С, не менее	180	170	150
10 Щелочность, *мг* КОН на 1 *г* не менее	4,0	2,0	2,0
11 Зольность, %, не менее	3,0	2,0	1,5
12 Механические примеси, %, не более	0,04	0,02	0,02
13 Вода, %	14 Отсутствие		

1) Additive 3) B
2) Type 4) V
5) Content, %, on lubricant
6) 100% calcium sulfonate
7) Oxidized petrolatum
8) Kinematic viscosity (cSt) at
9) Flash point (open crucible), °C, not below
10) Alkalinity, mg of KOH to 1 g, not below
11) Ash, %, not below
12) Mechanical impurities, %, not above
13) Water, % 14) None.

TABLE 5.72

Effectiveness of Petroleum Sulfonates as Corrosion Inhibitors [84]

1 Присадка	2 Концентрация * присадки, мас. %	3 Дизельное топливо прямой перегонки, содержащее 0,059% меркаптановой серы			
		4 сталь ст. 3		5 латунь ЛС-59	
		6 коррозия, г/м²	7 коэффициент защиты **, %	6 коррозия, г/м²	7 коэффициент защиты, %
8 Без присадки	—	2,6	—	0,56	—
9 НГ-102 (концентрат сульфоната кальция из масла АС-9,5)	0,05	0,34	87	—	—
10 Концентрат сульфоната кальция из масла АС-6,5	0,005	0	100	0,56	0
	0,01	0	100	0	100
	0,05	0	100	0	100
11 Концентрат сульфоната аммония из масла АС-9,5	0,005	1,59	39	—	—
	0,01	0,56	78	—	—
	0,05	0	100	0,79	0
12 Концентрат сульфоната аммония из масла АС-6,5	0,005	0	100	0,68	0
	0,01	0	100	0,68	0
	0,05	0	100	0	100
13 Концентрат сульфоната бария из масла АС-6,5	0,05	0	100	0,45	33
14 Концентрат сульфоната свинца из масла АС-6,5	0,05	0	100	0,23	66
15 Концентрат сульфоната натрия из масла АС-6,5	0,05	0	100	0,45	33
16 НГ-203А (концентрат сульфоната кальция из масла АС-6,5)	0,01	0,68	74	—	—

*Converted to active part.

**Difference between 100% and ratio of amount of corrosion with additive to amount without additive, expressed in %.

1) Additive
2) Concentration* of additive, % by mass
3) Straight-run diesel fuel containing 0.059% mercaptan sulfur
4) Steel St. 3
5) Brass LS-59
6) Corrosion, g/m²
7) Coefficient of protection,** %
8) Without additive
9) NG-102 (concentrate of calcium sulfonate from oil AS-9.5)
10) Calcium sulfonate concentrate from oil AS-6.5
11) Ammonium sulfonate concentrate from oil AS-9.5
12) Ammonium sulfonate concentrate from oil AS-6.5
13) Barium sulfonate concentrate from oil AS-6.5
14) Lead sulfonate concentrate from oil AS-6.5
15) Sodium sulfonate concentrate from oil AS-6.5
16) NG-203A (calcium sulfonate concentrate from oil AS-6.5).

Fuels which in unsaturated hydrocarbons are usually stabilized with antioxidants (or metal deactivators), which also act to some extent as corrosion inhibitors, retarding the formation of aggressive hydrocarbon-oxidation products.

In the fuel, corrosion inhibitors act by one of the following mechanisms: a) as surface-active compounds, forming a protective film on the metal by oriented adsorption of polar groups; b) they have a neutralizing effect on acidic aggressive products; c) they react chemically with the metal to form a protective film on its surface.

Rust inhibitors, which prevent corrosion of metals by fuel in the presence of water, are most commonly used.

Various chemical compounds have been suggested as corrosion inhibitors: esters, diesters, amines, metal naphthenates, petroleum sulfonates, organic acids and their salts, hydroxycarboxylic acid, etc. Application of corrosion inhibitors to sulfur-containing fuels is most important for domestic practice.

Tables 5.70 and 5.71 give physicochemical properties of certain sulfonate-base additives.

TABLE 5.73

Protection of Steel and Brass from Corrosion by Sulfur-Containing Diesel Fuels on Addition of Calcium Sulfonate [84]

1 Показатели	2 Без присадки	3 Концентрат сульфоната кальция КСК из масла АС-6,5		4 Концентрат сульфоната аммония КСА из масла АС-6,5	
5 Концентрация присадки, мас. %	—	0,005	0,01	0,01	0,05
6 Дизельное топливо прямой перегонки, содержащее 0,01% меркаптановой серы:					
7 Сталь Ст. 3					
8 коррозия, г/м²	1,2	0	0	0	—
9 коэффициент защиты, %	—	100	100	100	—
10 Сталь ШХ-15:					
8 коррозия, г/м²	0,68	0	0	0	—
9 коэффициент защиты, %	—	100	100	100	—
11 Латунь ЛС-59:					
8 коррозия, г/м²	0.45	0	0	0,23	—
9 коэффициент защиты, %	—	100	100	49	—
12 Дизельное топливо, содержащее 20% компонента каталитического крекинга с 0,03% меркаптановой серы:					
7 Сталь Ст. 3					
8 коррозия, г/м²	3,63	0,23	0	—	0
9 коэффициент защиты, %	—	94	100	—	100
11 Латунь ЛС-59					
8 коррозия, г/м²	0,68	—	0	—	0
9 коэффициент защиты, %	—	—	100	—	100

1) Index
2) Without additive
3) KSK calcium sulfonate concentrate from oil AS-6.5
4) KSA ammonium sulfonate concentrate from oil AS-6.5
5) Additive concentration, % by mass

6) Straight-run diesel fuel containing 0.01% mercaptan sulfur
7) Steel St. 3
8) Corrosion, g/m^2
9) Coefficient of protection, %
10) Steel ShKh-15
11) Brass LS-59
12) Diesel fuel containing 20% catalytic cracking component with 0.03% mercaptan sulfur.

The effectiveness of petroleum sulfonates as corrosion inhibitors depends on the composition of the sulfo acids and the metal in the sulfonate (Table 5.72). The best sulfonates are obtained by sulfonating AS-5 and AS-6.5 oils; sulfonates made from higher-viscosity oils, which are known as highly efficient wetting additives to oils, are inferior to the low-molecular sulfonates as corrosion inhibitors. Sulfonates made from gas oils or kerosenes are insoluble in fuels. The most effective corrosion inhibitors are calcium and ammonium sulfonates. Calcium sulfonate protects both steel and brass well.

Table 5.73 indicates the action of sulfonate additives when used in various sulfur-containing diesel fuels in concentrations of 0.01-0.05% by mass of the sulfonate.

Calcium and ammonium sulfonates are produced as concentrates (KSK and ASK) in oil; the sulfonate content in the concentrate is ∿25%. Commercial NG-203 protective lubricant may be used as a corrosion inhibitor in sulfur-containing diesel fuel; in addition to the sulfonate, it contains ∿50% of oxidized petrolatum.

Effective corrosion inhibitors are produced from nitrated oils [85]. The additive contains 12-15% of nitroalkylaromatic compounds. It offers good corrosion protection for steel, but is less effective than sulfonate in the protection of brasses.

Additives that Reduce Varnish and Deposit Buildup and Wear in the Engine's Cylinder-Piston Group

These additives are designed for addition to sulfurous and high-sulfur diesel fuels. Their action is based on neutralization of the aggressive combustion products of sulfur-containing fuels (sulfur oxides, chiefly the trioxide) or on their conversion into nonaggressive products. Amines, nitrates and carbonates of alkali metals, metal naphthenates, organic phosphites, and others have been proposed as such additives.

Oil additives have the major role in reducing deposits and wear in the cylinder-piston group of the engine when sulfur fuels are used; however, when the additive is used directly in the fuel, a substantial additional gain is achieved.

For stationary engines, the problem is solved by using gaseous ammonia as a neutralizing agent; it is fed directly into the engine's induction system [86] (Fig. 5.35).

Foreign additives intended to reduce deposit buildup and wear

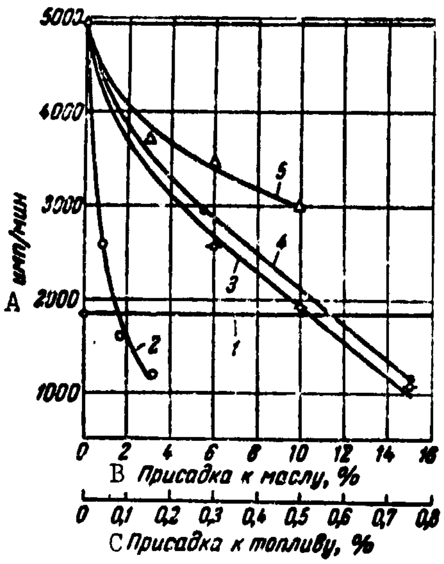


Fig. 5.35. Comparative effectiveness of ammonia and oil additives in reducing piston-ring wear in 24-8.5/11 engine in operation on fuel containing 1.6% by mass of sulfur: 1) DS fuel; 2) NH_3; additives: 3) VNII NP-360; 4) MNI NP-22k; 5) TsIATIM-339. A) Impulses//min; B) oil additive, %; C) fuel additive, %.

in the engine's cylinder-piston group (Dislip, Fuelslip, Territe and a number of others) are recipes that incorporate naphthalene homologues, metal-organic compounds, and amines.

Additives that Reduce Vanadium Corrosion

To suppress vanadium corrosion and reduce deposits, additives whose action is based chiefly on their ability to form high-melting compounds with the vanadium oxides present in fuel combustion products, thus eliminating the corrosive action of vanadium oxides, are added to fuels used in gas turbines [87]. Various compounds that change the nature of the deposits formed on turbine parts, although they influence the amount of these deposits to a lesser degree, have been proposed for use as such additives.

TABLE 5.74

Composition of Certain Additives Against Vanadium Corrosion

1 Присадки	2 Общая формула или состав
3 Магнезит	MgO, $MgSO_4$, $MgCl_2$ 4(до 92% MgO)
5 Кальцит	$CaCO_3$
6 Доломит	$CaMg(CO_3)_2$: 30,4% CaO, 21,7% MgO, 47,9% CO_2
7 Окись алюминия	Al_2O_3
8 Марисаллит	9 Разновидность кварца (SiO_2)
10 Каолин	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ или 11 $Al_4(Si_4O_{10})(OH)_8$: 39,5% Al_2O_3, 46,5% SiO_2, 14% H_2O
12 Монтмориллонит	$m(Mg_3[Si_4O_{10}][OH]_2 \cdot 11H_2O)p((Al, Fe)_2Si_4O_{10}(OH)_2)$ $m : p = 0,8$—$0,9$

1) Additive
2) Empirical formula or composition
3) Magnesite
4) Up to
5) Calcite
6) Dolomite
7) Aluminum oxide
8) Marisallite
9) A variety of quartz
10) Kaolin
11) Or
12) Montmorillonite.

TABLE 5.75

Effectiveness of Magnesium Sulfate in Reducing Vanadium Corrosion [89]

1 Сталь	2 Изменение веса пластинки в присутствии					
	3 ванадия		4 ванадия и магния (1 : 1,5)		4 ванадия и магния (1 : 3)	
	%	г/м²	%	г/м²	%	г/м²
5 ЭИ481	0,170	20,7	0,039	4,6	0,037	4,2
ЭИ607	0,096	11,8	0,040	4,9	0,052	3,0
ЭИ417	0,160	18,6	0,120	14,2	0,067	7,8
ЭИ612	0,066	8,6	0,042	5,6	0,033	4,8
ЭИ726	0,058	7,2	0,028	3,4	0,040	4,9

1) Steel
2) We:.ȷht change of plate in presence of
3) Vanadium
4) Vanadium and magnesium
5) EI481.

Since the amount of sulfur in mazouts is always considerably greater than that of vanadium, those metals whose sulfates are thermally less stable than vanadates can be used as effective additives, since otherwise the metal will be bound in the form of the sulfate and will not be able to act on the vanadium. Thus, calcium, magnesium and zinc are more effective than barium, since their sulfates are less stable. Silicon compounds and aluminum silicates are highly effective as vanadium-corrosion inhibitors.

Methods of introducing the additives vary; they may be injected in the form of a suspension, paste or aqueous solution or dissolved in the fuel or injected into the flame in the form of finely divided particles.

Various natural compounds of silicon, magnesium, and aluminum, as well as magnesium oxide and sulfate, have been tested successfully as additives to domestic fuels [88, 89]. Table 5.74 presents some of the compounds and Table 5.75 test results for magnesium sulfate.

Considerable interest attaches to residual-fuel-soluble magnesium compounds that have been proposed for use against vanadium corrosion, e.g., magnesium naphthenate, magnesium salts of synthetic fatty acids with C_{17}-C_{20}, and oxidized petrolatum [90]. When these products are added to a sulfur-containing mazout with $3.7 \cdot 10^{-3}$% vanadium, vanadium corrosion is reduced (Figs. 5.36 and 5.37).

VNII NP-102 additive and its modification, VNII NP-103, have been proposed for use against coating of boiler heating surfaces and control of sedimentation in storage tanks.

Rear heating surfaces of boiler installations can be protected from corrosion in operation on high-sulfur fuels with the

aid of additives that reduce the content of SO_3 in the combustion products and lower the dew point. Dolomite and silica in amounts of 0.1-0.2% by mass on the fuel reduce corrosion markedly, since deposits form on the heating surfaces in considerably smaller amounts and their structure is modified. These additives have an insignificant effect as regards lowering dew point. Better results are obtained with the use of additives that react chemically with SO_3 – zinc, magnesium, and ammonium compounds. These additives depress the dew point of the smoke gases and inhibit corrosion considerably.

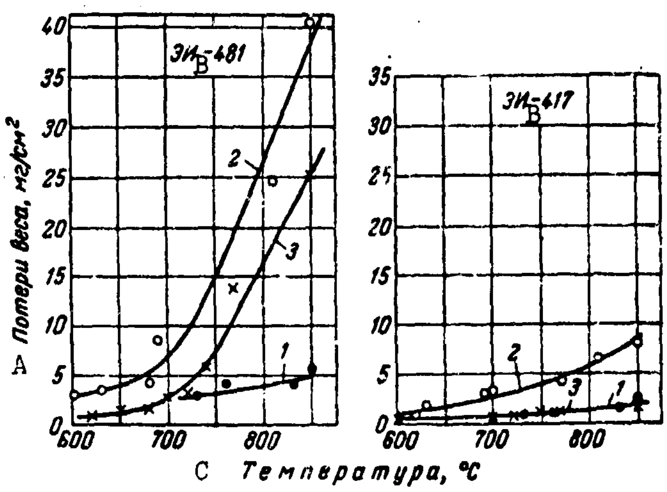


Fig. 5.36. Decrease in vanadium corrosion of high-temperature steels on introduction of 0.2% magnesium salts of oxidized petrolatum into Fs-5 mazout (vanadium content $4 \cdot 10^{-3}$%). 1) Fs-5 mazout with additive; 2) Fs-5 mazout without additive; 3) F-12 mazout (no vanadium content). A) Weight loss, mg/cm²; B) EI-481; C) temperature, °C.

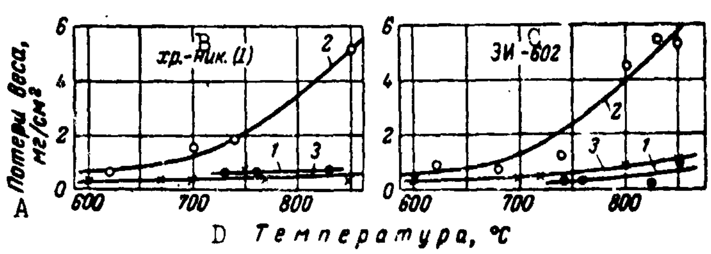


Fig. 5.37. Decrease in vanadium corrosion of high-temperature nickel steels on introduction of 0.2% magnesium salts of oxidized petrolatum into Fs-5 mazout (key same as in Fig. 5.36). A) Weight loss, mg/cm²; B) chromium-nickel (I); C) EI-602; D) temperature, °C.

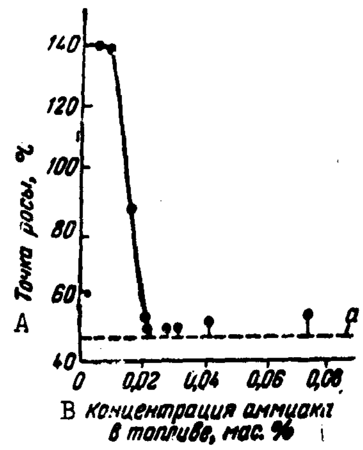


Fig. 5.38. Variation of dew point as a function of ammonium concentration. A) Dew point, °C; B) ammonia concentration in fuel, % by mass.

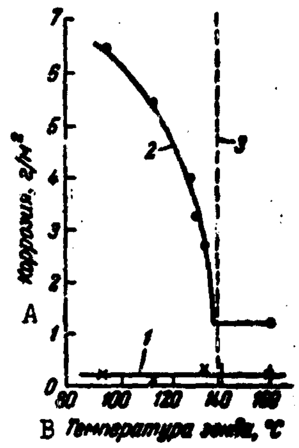


Fig. 5.39. Change in corrosion with and without ammonia injection: 1) with ammonia injection; 2) without ammonia; 3) dew point 139°C (without ammonia). A) Corrosion, g/cm²; B) probe temperature, °C.

When ammonia is injected into the firebox at 300°C in a concentration of 0.021% by mass, the dew point of pure water vapor is reached. Figures 5.38 and 5.39 show curves of the dew point as a function of ammonia concentration and the curve of corrosion rate with and without ammonia injection as a function of temperature [91].

To prevent sulfuric-acid corrosion at wall temperatures below the dew point, a British firm has patented (British Patent 73,490) the additive "Teramine," which is a mixture of tertiary heterocyclic amines obtained from coal tar. In the atomized state, 0.03-0.05% by mass of Teramine is injected into the fuel in the boiler gas duct at a point where the gas temperature is ~250°C. In addition to reducing rear-surface corrosion, Teramine raises boiler efficiency by 1.5% by lowering exhaust-gas temperature.

5. ADDITIVES THAT FACILITATE USE OF FUELS AT LOW TEMPERATURES

Additives of this group include substances that make it possible to eliminate operating difficulties when fuels are used during the cold season or at high altitude.

Antiicing additives are added to automotive gasolines to prevent carburetor icing. The additives also prevent water from freezing in fuel pumps and tanks. Antiicing additives in use include isopropyl alcohol, ethylene glycol monobutyl ester (concen-

tration 0.05-0.5% by mass), dimethylcarbinol, glycerine monooleate, certain amines and ammonium phosphates [3].

Additives that Lower Fuel Crystallization Temperatures (Depressors)

Depressor additives are designed for addition to paraffin-base diesel fuels, which have high crystallization temperatures. They have almost no effect on the cloud points of the fuels, but they do lower its pour point substantially, i.e., they do not inhibit the onset of solid-hydrocarbon crystallization, but they do retard crystal growth. As they are adsorbed onto minute paraffin crystals, they prevent their growth and formation of a crystal lattice; this inhibits adsorption of liquid hydrocarbons by the paraffin with formation of a gel.

TABLE 5.76

Physicochemical Properties of Commercial Depressors (from AUSS 8443-57 and VTU NP 14-58)

1 Показатели	2 АзНИИ	3 ОПД	
		1	2
4 Снижение температуры застывания масла, °С, не менее:			
5 АК-15 при добавлении 0,1% депрессора . .	10	—	—
6 базового при добавлении 3% ОПД . . .	—	18	18
7 Коксуемость, %, не более	3,5	—	—
8 Зольность, %, не более . .	0,2	—	—
9 Водорастворимые кислоты и щелочи	10 Отсутствие	—	—
11 Механические примеси, %, не более	0,15	—	—
12 Вода	10 Отсутствие	—	—
13 Цвет	—	14 От темно-желтого до светло-коричневого	15 От темно-желтого до темно-коричневого
16 Кислотное число, мг КОН на 1 г	—	46—65	50—70
17 Коэффициент омыления, не менее	—	115—165	125—175
18 Отношение коэффициента омыления к кислотному числу, не менее	—	2,5	2,5

1) Index
2) AzNII
3) OPD
4) Oil pour point depression, °C, not less than
5) AK-15 with 0.1% depressor
6) Base with 3% OPD
7) Coking capacity, %, not above
8) Ash, %, not above
9) Water-soluble acids and alkalies
10) None
11) Mechanical impurities, %, not above
12) Water
13) Color
14) From dark yellow to light brown
15) From dark yellow to dark brown
16) Acid number, mg of KOH to 1 g
17) Saponification coefficient, not below
18) Ratio of saponification coefficient to acid number, not below.

TABLE 5.77

Influence of AzNII Depressor on Low-Temperature Properties of Diesel Fuels [75]

1 Топливо	2 Концентрация присадки, мас. %	3 Температура, °С	
		4 помутнения	5 застывания
6 Дизельное			
7 летнее	—	−6	−12
летнее	0,2	−7	−26
летнее	0,5	−8	−28
летнее	1,0	−10	−32
8 зимнее	—	−49	9 −66
зимнее	0,5	−53	Ниже −70
10 Газойль сураханский			
11 тяжелый	—	+5	−16
тяжелый	1,0	0	−25
12 легкий	—	−4	−7
легкий	1,0	−7	−25
13 Смесь 60% сураханского солярового дистиллята и 40% сураханского керосина	—	+1	−4
14 То же	1,0	−1	−31
15 Смесь 60% сураханского солярового дистиллята и 40% доссорского керосина	—	0	−5
14 То же	1,0	−3	−50

1) Fuel
2) Additive concentration, % by mass
3) Temperatures, °C
4) Cloud point
5) Pour point
6) Diesel
7) Summer
8) Winter
9) Below
10) Surakhany gas oil
11) Heavy
12) Light
13) Mixture of 60% Surakhany solar distillate and 40% Surakhany kerosene
14) Same
15) Mixture of 60% Surakhany solar distillate and 40% Dossor kerosene.

The same additives as are used in lubricating oils may be used as depressors in fuels, namely: condensation products of nonpolar organic compounds, e.g., of naphthalene with chlorinated paraffin (AzNII depressor); products of voltolization – voltols, soaps of multivalent cations, oxidation products of macromolecular hydrocarbons, products of condensation of nonpolar compounds with polar compounds, etc.

Depressor concentrations in the fuel range from 0.01–0.5–1.0% by mass, depending on the type of additive and fuel. Tables 5.76 and 5.77 list the physicochemical properties of industrial depressors and their influence on the pour points of diesel fuels.

AzNII commercial depressor is produced by condensing naphthalene with two molecules of a chlorinated paraffin in the presence of aluminum chloride. OPD depressor is obtained by oxidizing petrolatum.

Additives that Prevent Formation of Ice Crystals in Fuels

These additives are used in aviation fuels (gasolines, kerosenes). Their action is based on the formation of low-freezing mixtures with water, which prevents separation of water from the fuel in the form of ice crystals. The additive concentrations in the fuel range from 0.1 to 1.0% by mass.

Isopropyl, methyl, and ethyl alcohols, tetra-, penta- and hexaethylene glycols, methyl and ethyl esters of ethylene glycol, and other compounds have been used for these purposes [1, 75, 99].

One of the most effective additives is ethyl cellosolve — the monoethyl ester of ethylene glycol (AUSS 8313-60), the physicochemical properties of which we list below:

External appearance	Colorless transparent liquid
Density ρ_4^{20}	0.930-0.935
Fractional composition:	
distills below 128°C, % by mass, not more than	2
distills in 128-138°C temperature range, % by mass, no less than	94
residue, % by mass, no more than	3
losses, % by mass, no more than	1
Refractive index for product, n_D^{20}	1.4070-1.4090
Saponification number, mg of KOH to 1 g, not above	2.5
Acidity (converted to acetic acid), % by mass, not above	0.01
Ethyl cellosolve content in product, % by mass, not below	95.0
Dry residue, % by mass, not above	0.005
Water, % by mass, not above	0.5

Addition of ethyl cellosolve to jet fuels in concentrations of 0.1-0.3% completely eliminates formation of ice crystals at all temperatures encountered in winter operation (Tables 5.78 and 5.79).

Since ethyl cellosolve dissolves better in water than in fuels, it may be "washed out" of the fuel when the latter comes into contact with water (for example, during shipment of the fuel). For this reason, it is not added to the fuel at the refineries, but directly at the points of application. Ethyl cellosolve does not cause moisture to accumulate in the fuel during storage (Table 5.80). Ethyl cellosolve has been used in the USSR since 1955-1956 in aviation fuels (jet fuels and aviation gasolines) [93].

The additive PF A-55 MB [92] (Table 5.81) has been in use in the USA since 1957-1960 as a preventative of ice-crystal formation. This additive is a mixture of about 99.6% methyl cellosolve and 0.4% glycerine [94]. It is used in military aviation for JP-4

TABLE 5.78

Rate of Solution of Ice Crystals in Fuel when Ethyl Cellosolve is Added [93]

1 Содержание этилцеллозольва, %	2 Количество снега, введенного в топливо, %	3 Этилцеллозольв вводился в топливо, содержащее снег			5 Снег вводился в топливо, содержащее этилцеллозольв		
		4 Время растворения кристаллов льда (в мин) при температуре					
		−5° C	−20° C	−30° C	−5° C	−20° C	−30° C
0,1	0,05	—	—	—	5	11	23
	0,1	—	—	—	25	41	65
0,3	0,05	3	8	21	2	6	15
	0,1	10	25	46	8	21	41

1) Ethyl cellosolve content, %
2) Amount of snow introduced into fuel, %
3) Ethyl cellosolve introduced into fuel containing snow
4) Time to dissolve ice crystals (in min) at temperature of
5) Snow introduced into fuel containing ethyl cellosolve.

TABLE 5.79

Effectiveness of Ethyl Cellosolve Against Formation of Ice Crystals in Fuels [93]

1 Топливо	2 Содержание этилцеллозольва, %	3 Температура (в °C) образования кристаллов льда при содержании воды в топливе, %									
		0,001	0,002	0,003	0,004	0,005	0,007	0,009	0,01	0,011	0,013
Т-1	0	4 до −60 кристаллов нет	−60 5 кристаллы	−40 5 кристаллы	—	−30 5 кристаллы	—	—	—	—	—
	0,05	6 То же	до −60 кристаллов нет 4		−60 5 кристаллы	−50 5 кристаллы	—	—	—	—	—
	0,1	»	6 То же	То же 6 4	до −60 кристаллов нет	5 −60 кристаллы	5 −50 кристаллы	−40 5 кристаллы	—	—	—
	0,3	»	»	»	6 То же	до −60 4 кристаллов нет					
ТС-1	0	»	−60 5 кристаллы	—	−40 5 кристаллы	—	5 −15 кристаллы	—	—	— —	— —
	0,05	—	—	—	—	5 −55 кристаллы	—	−40 5 кристаллы	—	—	—
	0,1	—	—	—	—	4 до −60 кристаллов нет		−55 кристаллы	−50 5 кристаллы	—	—
	0,3	—	—	—	—	—	— 5	4 до −60 кристаллов нет			
ТС-2	0	—	−60 5 кристаллы	—	−50 5 кристаллы	−40 5 кристаллы	5 −25 кристаллы	—	—	—	—
	0,1	—	—	—	—	—	—	−60 5 кристаллы	—	−45 5 кристаллы	—
	0,3	—	—	—	—	—	—	—	до −60 кристаллов нет 4		

1) Fuel
2) Ethyl cellosolve content, %
3) Temperature of formation of ice crystals (°C) at fuel water content of ... %
4) No crystals to -60
5) Crystals at -60
6) Same.

fuel [95], and is also added to kerosene-type fuels; it also finds use in civil aviation.

TABLE 5.80

Change in Water Content in Fuels with 0.3% Ethyl Cellosolve during Long-Term Storage [93]

1 Топлива	2 Содержание этилцеллозольва в топливе, %	3 Содержание воды в топливе (в %) через							
		4 исходное (январь)	5 1 месяц	5 3 месяца	5 5 месяцев	5 6 месяцев	5 7 месяцев	5 10 месяцев	5 12 месяцев
Т-1	—	0,0033	0,0035	0,0048	0,0083	0,0076	0,0088	0,0044	0,0036
6 То же	0,3	0,0053 *	0,0031	0,0051	0,0083	0,0065	0,0092	0,0060	0,0039
7 ТС-1	—	0,0041	0,0043	0,0058	0,0095	0,0096	0,0113	0,0075	0,0049
6 То же	0,3	0,0066 *	0,0047	0,0061	0,0093	0,0099	0,0111	0,0073	0,0046
8 Б-95/130	—	0,0081	0,0076	0,0095	0,0131	0,0138	0,0163	0,0101	0,0075
6 То же	0,3	0,0096 *	0,0081	0,0093	0,0140	0,0130	0,0156	0,0105	0,0081

*The higher water content in the original fuels with 0.3% ethyl cellosolve is explained by the fact that 0.6-0.7% water was present in the ethyl cellosolve itself. Subsequently, the water introduced into the fuel with the ethyl cellosolve transfers to the air; passage of moisture from the fuel to the air and back (depending on atmospheric conditions) also explains the fluctuations in fuel moisture content during storage.

1) Fuel
2) Ethyl cellosolve content in fuel, %
3) Water content in fuel (in %) after
4) Initial (January)
5) Month(s)
6) Same
7) TS-1
8) B-95/130.

TABLE 5.81

Influence of PF A-55 MB Additive on Ice-Crystal Formation in Jet Fuels [92]

1 Топливо	2 Температура, при которой забивается фильтр, °C		
	3 без присадки	4 0,05% присадки	4 0,1% присадки
5 IP-4 с 0,01% воды	6 от −11 7 до −9	—	−60
IP-4 с 0,08% »	от −2 до −1	—	−60
IP-5 с 0,08% »	−8	−25	−51

1) Fuel
2) Temperature at which filter is clogged, °C
3) Without additive
4) ...% additive
5) IP-4 with 0.01% water
6) From
7) To.

6. OTHER FUEL ADDITIVES

In addition to the additives mentioned above, dyes, color stabilizers, additives that prevent accumulation of static electricity, and certain others are added to fuels.

Dyes

Dyes are added to gasolines for identification purposes. The color of a gasoline indicates that it contains a certain additive that improves its basic operational properties (antiknock, antioxidant, etc.). The dyes themselves have negligible contents in the gasoline and no influence on their properties.

TABLE 5.82

Physicochemical Properties of Certain Commercial Dyes for Gasolines

1 Краситель	2 Температура плавления, °C, не менее	3 Содержание золы, %, не более	4 Содержание влаги, %, не более
5 Судан			
6 желтый Ж	157	—	—
7 красный Ж	194	4	2
8 красный С	174	8	3
9 Оранжевый	127	—	1

1) Dye
2) Melting point, °C, not below
3) Ash content, %, not above
4) Moisture content, %, not above
5) Sudan
6) Yellow Zh
7) Red Zh
8) Red S
9) Orange.

Gasolines containing TEL are colored red and pink (A-66) or blue and green (A-76); aviation gasolines are yellow (B 95/130) or bright orange (B 100/130). The Sudans - azo dyes that are soluble in hydrocarbons and insoluble in water - are the principal gasoline dyes (Table 5.22).

Additives Against Accumulation of Static Electricity

Additives to counter the accumulation of static electricity ("antistatics") are added to distillate fuels (gasolines, kerosenes, diesel fuels) to raise their conductivities to a safe level.

TABLE 5.83

Concentrations of Certain Additives Necessary to Attain 1000-picoohm/m Conductivity in Hydrocarbons [96]

1 Топливо	2 Присадка	Концентрация, кг на 1000 м³ 3
4 Бензол	5 Тетраизоамилпикриновокислый аммоний	53
6 Лигроин	Олеат марганца 7	293
8 Бензин	Раствор кальциевой соли ди-(2-этил-гексил) 9 сульфосукциниловой кислоты (Са-аэрозоль)	2000
4 Бензол	Диизопропилсалицилат кальция 10	2400
8 Бензин	Раствор хромовой соли смеси моно- и диалкилсалициловых кислот (Cr-AC) 11	6,2
»	Антистатическая фирмы «Шелл» 12	2

1) Fuel
2) Additive
3) Concentration, kg to 1000 m^3
4) Benzene
5) Ammonium tetraisoamyl picrate
6) Ligroin
7) Manganese oleate
8) Gasoline
9) Solution of calcium salt of di-(2-ethylhexyl)sulfosuccinic acid (Ca aerosol)
10) Calcium diisopropylsalicylate
11) Solution of chromium salt of mixture of mono- and dialkylsalicylic acids (Cr-AC)
12) Shell antistatic.

Petroleum products with conductivities above 1000 picoohms/m [3] are safe as regards accumulation of static-electricity charges that might result in explosions during pump transfers. A conductivity as low as 500 picoohms/m is not dangerous [96].

Table 5.83 gives the concentrations of certain additives necessary to ensure the required conductivity in fuels. The Ca-aerosol additive contains 2% by mass of calcium, 55% of a neutral solvent; its average molecular weight is ~2000.

Cr-AC additive contains chromium salts of mono- and dialkylsalicylic acids whose alkyl chains consist of 14 to 18 carbons;

[3]/393

the additive contains 2.1% by mass of chromium and 30% of a neutral solvent; its average molecular weight is ∿2500.

The American firm Shell recommends a mixture of equal quantities of the Ca-aerosol-OT and Cr-AC additives for the trade, since the synergistic action of the additive mixture is more effective than either taken separately. Addition of this additive in an amount of 2 kg to 1000 m³ is recommended for all fuels.

The use of additives that increase fuel conductivity does not eliminate the need for grounding tanks, since the additives prevent only those cases of static-electricity explosions in which the cause is low fuel conductivity.

Additives that Improve Antiwear Properties of Fuels

The antiwear properties of fuels, on which the service life and operating reliability of fuel pumps and aviation gas-turbine engines depend, can be improved with additives. When certain additives (fatty acids, phenols, etc.) are added to T-2 low-viscosity fuel in amounts of 0.01-0.05% by mass, its antiwear properties are brought up to the level of T-1 and TS-1 fuels (Tables 5.84-5.86).

TABLE 5.84

Antiwear Properties of T-2 Fuel* Containing 0.01% by mass of Narrow Fatty-Acid Fractions (t = 20°C) (after A.V. Vilenkin, G.I. Kichkin, K.I. Klimov and I.V. Rozhkov)

1 Фракция	2 Кислотное число фракций, мг KOH на 1 г	3 Нагрузка $P_{кр}$ по стенду КВ-1, кГ	1 Фракция	2 Кислотное число фракций, мг KOH на 1 г	3 Нагрузка $P_{кр}$ по стенду КВ-1, кГ
C_{10}	327	17,6	C_{17}	209	29,5
$C_{11}-C_{13}$	280	19,7	C_{18}	197	34,0
$C_{14}-C_{15}$	240	21,2	C_{19}	187	36,5
C_{15}	232	21,2	C_{20}	178	>40
C_{16}	217	25,6			

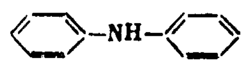
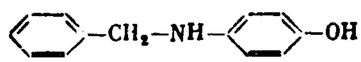
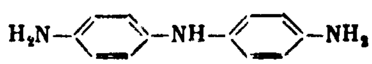
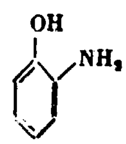
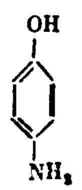
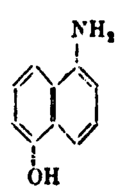
*Antiwear properties without additive P_{kr} = = 10.8 kg.

1) Fraction
2) Acid number of fraction, mg of KOH to 1 g
3) Load P_{kr} on KV-1 stand, kg.

Additives also improve the antiwear properties of fuels at elevated temperatures (Table 5.87). Added in small concentrations (0.01% by mass), special antiwear additives developed for oils raise the antiwear properties of fuels to about the same level as the antioxidants introduced into the fuel.

TABLE 5.85

Antiwear Properties of T-2 Fuel* Containing 0.01% by mass of Aromatic Amines and Aminophenols (t = 20°C) (after A.V. Vilenkin, G.I. Kichkin, K.I. Klimov and I.V. Rozhkov)

1 Присадка	2 Химическое строение	Нагрузка $P_{кр}$ по стенду КВ-1, кГ 3
4 Дифениламин		13,4
5 Бензил-*п*-аминофенол		17,4
6 Диаминодифениламин		11,8
7 *о*-Аминофенол		15,2
8 *п*-Аминофенол		19,0
9 1,5-Аминонафтол		17,4

*Antiwear properties without additive P_{kr} = = 11.8 kg.

1) Additive
2) Chemical structure
3) Load P_{kr} on KV-1 stand, kg
4) Diphenylamine
5) Benzyl-p-aminophenol
6) Diaminodiphenylamine
7) o-Aminophenol
8) p-Aminophenol
9) 1,5-Aminonaphthol.

TABLE 5.86

Antiwear Properties of T-2 Fuel* with Phenol-Type Additives (t = 20°C) (after A.V. Vilenkin, G.I. Kichkin, K.I. Klimov and I.V. Rozhkov)

1 Присадки	2 Нагрузка $P_{кр.}$ (в кГ) по стенду КВ-1 при содержании присадки, вес. %	
	0,05	0,1
3 2,6-Ди-*трет*-бутил-4-метилфенол	18,5	—
4 α-нафтол	18,6	—
5 β-нафтол	17,3	—
6 *н*-Бутилфенол	—	13,0
7 Технические фенолы ФЧ-16	20,0	—
8 Древесно-смольный антиокислитель		
9 сорта A	—	16,6
10 сорта B	—	14,5
11 Пиролизат древесной смолы	16,0	—
12 Сланцевые фенолы (фракция 200—300° C)	—	15,4

*Antiwear properties without additive P_{kr} = = 12.8 kg.

1) Additive
2) Load P_{kr} (kg) on KV-1 bench with additive content of ...% by mass
3) 2,6-Di-*tert*-butyl-4-methylphenol
4) α-naphthol
5) β-naphthol
6) *n*-Butylphenol
7) FCh-16 technical phenols
8) Wood-tar antioxidant
9) Grade A
10) Grade B
11) Wood-tar pyrolyzate
12) Shale phenols (200-300°C fraction).

TABLE 5.87

Influence of Additives on Antiwear Properties of TS-1 Fuel at 110°C [97]

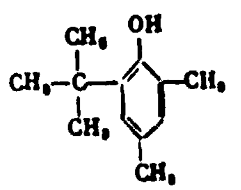
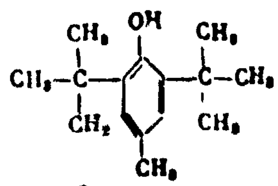
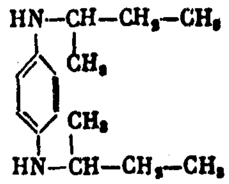
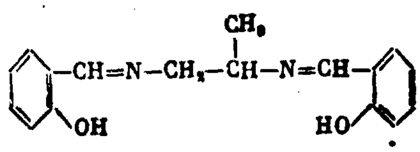
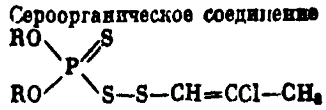
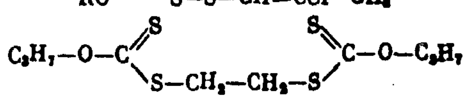
a № пп.	b Присадка	c Структурная формула	d [illegible]	e $P_{кр}$, [illegible]
1	Топливо без присадки	—	—	10,7
	А. Антиокислители			
2	2,4-Диметил-6-*трет*-бутилфенол		0,01	16,2
3	2,6-Ди-*трет*-бутил-4-метилфенол		0,01	16,4

TABLE 5.87 (Continued)

a № пп.	b Присадка	c Структурная формула	d Концентрация, мас. %	e $P_{кр}$, кг
4	N, N'-Ди-*втор*-бутил-*п*-фенилендиамин		0,01	17,4
	B. Деактиватор металлов			
5	1,2-Дисалицилиденпропилендиамин		0,001	12,8
	C. Противоизносные присадки для масел			
6	В-15/2А	Сероорганическое соединение	0,01	20,3
7	ЛЗ-309		0,01	16,9
8	ЛЗ-23К		0,01	19,1

a) No.
b) Additive
c) Structural formula
d) Concentration, % by mass
e) P_{kr}, kg
1) Fuel without additive
A) Antioxidants
2) 2,4-Dimethyl-6-*tert*-butylphenol
3) 2,6-Di-*tert*-butyl-4-methylphenol
4) N,N'-Di-*sec*-butyl-*p*-phenylenediamine
B) Metal deactivator
5) 1,2-Disalicylidenepropylenediamine
C) Antiwear additives for oils
6) V-15/2A; sulfur-organic compound
7) L3-309
8) L3-23K.

REFERENCES

1. Petroleum Products Handbook, McGraw-Hill Book Co., New York-Toronto-London, 1960.

2. Read, A., Armed Forces Chem. J., 13, No. 6, 43-50, 60 (1959).

3. Kirk, J.H., Yong, H.D., Petro. Ref., No. 9, 203, 209 (1959); Herbst, Ibid., page 203.

4. Frey, I.J., World Petrol., 34, No. 8, 53, 15 (1963).

5. Korshak, V.V., Kolesnikov, G.S., Tetraetilsvinets [Tetraethyllead], Goskhimizdat, 1947.

6. Motornyye, reaktivnyye i raketnyye topliva [Motor, Jet and Rocket Fuels], Gostoptekhizdat, 1962.

7. Zabryanskiy, Ye.I., Zarubin, A.P., Detonatsionnaya stoykost' i vosplamenyayemost' motornykh topliv [Detonation Stability and Flammability of Motor Fuels], izd. "Khimiya," 1965.

8. Gureyev, A.A., Avtomobil'nyye benziny [Automotive Gasolines], Gostoptekhizdat, 1961.

9. Gureyev, A.A., Zarubin, A.P., Subbotin, A.P., Doklad na 7-i sessii po seraorganicheskim soyedineniyam [Paper at the 7th Session on Sulfur-Organic Compounds], izd. BashFAN, 1963.

10. Hanson, T.K., Coles, K.F., J. Inst. Petrol., 33, No. 286, 589 (1947).

11. Livings, H.K., Ind. Eng. Chem., 43, No. 3, 663 (1951).

12. Feygin, A.L., Alekseyeva, M.P., Eksperimental'noye issledovaniye vynositeley svintsa iz dvigatelya [Experimental Investigation of Engine Lead Scavengers] (Trudy TsIAM, No. 112), Oborongiz, 1946.

13. Hollowey, H., Bonnel, B., Ind. Eng. Chem., 37, No. 11 (1945).

14. Sablina, Z.A., Gureyev, A.A., Prisadki k motornym toplivam [Motor-Fuel Additives], Gostoptekhizdat, 1959.

15. Walters, E.L., Ind. Eng. Chem., 41, No. 5, 907 (1949).

16. Sabina, I.R., Mikita, I.I., Campbell, M.H., Proc. Am. Petrol. Inst., 33, 137 (1953).

17. Hirschler, D.A., McCullough, I.D., Hall, C.A., SAE Journal, 62, No. 1, 45 (1954).

18. Sturgis, B.M., SAE Trans., 6, 751 (1952).

19. Ninch, R.F., Automob. Ind., 15, 47 (1953).

20. Lovell, V., Gibson, Kh., Dzhons, B., IV Mezhdunarodnyy neftyanoy kongress [IV International Petroleum Congress], Vol. VII, Gostoptekhizdat, 1957.

21. Jeffrey, R.E., Griffith, L.W., Dunning, E., Boldwin, B., Petrol. Ref., 38, No. 8, 92 (1954).

22. Gibson, H.I., Petrol. Ref., 28, No. 6, 110 (1949).

23. Wilke, N., ATZ, 56, No. 7, 169 (1954).

24. Mikita, Dzh., Stardzhis, B.M., IV Mezhdunarodnyy neftyanoy kongress, Vol. VII, Gostoptekhizdat, 1955.

25. Richardson, W.L., Barusch, M.R., Kantsky, G.J., Steinke, R.E., Ind. Eng. Chem., 53, No. 4, 123/305 (1961).

26. Oil and Gas J., 58, No. 2 11/I, 30/50 (1960).

27. Hesselberg, H.E., Howard, I.R., SAE Trans., 69, 5 (1961).

28. Stormant, D.H., Oil and Gas, 60, No. 13 dated 26/III, 189, 192, 193, 195 (1962).

29. Automobile Eng., 50, No. 7, 29/287 (1960).

30. Automobile Eng., 50, No. 2, 13/53 (1960).

31. Nelson, W.L., Oil and Gas J., 60, No. 2 dated 8/I, 56/76 (1962).

32. Richardson, W.L., Barusch, M.R., Kautski, G.J., Steinke, R.E., J. Chem. Eng. Data, 6, No. 2, 305 (1961).

33. Perry, R.H., Gerard, P.L., Heath, D.P., SAE Journal, 70, No. 1, 48 (1962).

34. Richardson, W.L., Barusch, M.K., Steuart, W.T., Kautsky, G.J., Stone, R.K., J. Chem. Eng. Data, 6, No. 2, 309 (1961).

35. Oil and Gas J., 57, No. 5, 309 (1959).

36. Petrol. Ref., 38, No. 7, 149 (1959).

37. Neuman, S.R., Dille, K.L., Heisler, R.Y., Fontaine, M.F., SAE Annual. Meet. Preprints s.a., No. 12711 Ekspress-informatsiya, Avtomobilestroyeniye i avtotransport, No. 25 (1960).

38. Chem. Eng. News, No. 27, 7 (1957).

39. Chem. Eng. News, No. 28, 19 (1957).

40. U.S. Patent 2818417 (1957).

41. U.S. Patent 2380006 (1957).

42. USSR Author's Certificate 152526, 5 February 1962.

43. Gibson, Kh.Dzh., Lidzhett, U.B., Uorren, T., V neftyanoy kongress [V Petroleum Congress], Vol. IV, Gostoptekhizdat, 1961.

44. Collection "Novyy antidetonator dlya benzinov" [A New Antikrock for Gasolines] TsNIITEneftegaz, 1963.

45. Zaytsev, V., Lerner, M., Gureyev, A., Zabryanskiy, Ye.,

Kitskiy, B., Avtomobil'nyy transport, No. 1 (1962).

46. Braun, D.E., Lovell, G., Ind. Eng. Chem., 50, No. 10, 137-140 (1958).

47. Oil and Gas J., 57, No. 42, 49 (1959); 57, No. 47, 233 (1959).

48. Oil and Gas J., 57, No. 43, 82/122 (1959).

49. Oil and Gas J., 56, No. 19, 107 (1958).

50. Oil and Gas J., 58, No. 43, 126/154 (1960).

51. Gureyev, A.A., Zarubin, A.P., Subbotin, A.P., NNT, "Neftepererabotka" Series, No. 7 (1961).

52. Chem. Week, 76, No. 4, 54 (1955).

53. Cramer, P., Campbelle, J., Ind. Eng. Chem., 41, No. 5, 893 (1949).

54. Uhl, W.C., Nat. Petrol. New, 40, No. 25, 37 (1948).

55. Mapstone, G.E., Petrol. Eng., 26, No. 9, 23, Section C (1954).

56. Fayngar, M.M., Neft. khoz., No. 4, 5 (1937).

57. Borovaya, M.M., Khmel'nitskiy, Yu.D., Fish, Yu.L., Neft. khoz., No. 2 (1938).

58. Irlin, A.L., Neft. khoz., No. 3 (1938).

59. Ptashinskiy, I.A., Seledzhiyev, Yu.N., Neft. khoz., No. 2 (1938).

60. Filatov, V.V., Neft. khoz., No. 10 (1938).

61. U.S. Patent 2680756; 2680758; 2683157; 2694721; French Patent 1086656; 1083936; 1090321; 1091205; West German Patent 935467; Indian Patent 49769.

62. U.S. Patent 2023142; 2196447; 2203374; Netherlands Patent 33394; French Patent 720619; British Patent 393252.

63. Nottes, E.G., Erdol u. Kohle, 12, No. 8, 635-640 (1959).

64. Mapstone, G.E., Petrol. Eng., 26, No. 9, 23 (1954).

65. Roberti, K., Liparelli, Ye., III Mezhdunarodnyy neftyanoy kongress v Gaage [III International Petroleum Congress at The Hague], Vol. VII, 1951.

66. Delargey, R.I., Okie, I.P., Roberts, S.M., Chem. Eng., 55, No. 10, 124 (1948).

67. Brown, B.R., Ind. Eng. Chem., 47, No. 10, 2141 (1955).

68. Walch, A.D., Trans. Faraday Soc., 45, 1043 (1949).

69. Chamberlain, G.H., Walch, A.D., Proc. Roy. Soc., A-215, 175 (1949); Trans. Farad. Soc., 45, 1032 (1949).

70. Ragozin, N.A., Spravochnik po aviatsionnym i avtomobil'nym toplivam [Handbook of Aviation and Automotive Fuels], Gostoptekhizdat, 1940.

71. Hurn, R.W., Hughes, K.I., Ind. Eng. Chem., 48, No. 10, 1904 (1956).

72. Rozhkov, I.V., Vol'f, M.B., Kornilova, Ye.N., NNT, "Neftepererabotka" Series, No. 6 (1957).

73. Robins, W.G., SAE Quart. Trans., No. 5 (1951).

74. Schonwalder, Erdöl u. Kohle, No. 7, 78 (1954).

75. In collection "Motornyye, reaktivnyye i raketnyye topliva" [Motor, Jet and Rocket Fuels], Chapter XIV, Gostoptekhizdat, 1962.

76. Tilicheyev, M.D., Proizvodstvo drevesno-smolyanogo antiokislitelya [Production of Wood-Tar Antioxidant], Gostoptekhizdat, 1943.

77. Rozhkov, I.V., Sablina, Z.A., Gureyev, A.A., Kornilova, Ye.I., in collection "Prisadki k maslam i toplivam" [Oil and Fuel Additives], Gostoptekhizdat, 1961.

78. Gureyev, A.A., Sablina, Z.A., Silishchenskaya, N.M., Sobolev, Ye.P., Subbotin, A.P., Khimiya i tekhnologiya topliv, No. 12 (1962).

79. Rozhkov, I.V., Kornilova, Ye.N., Englin, B.A., Azerb. neft. khoz., No. 1 (1958).

80. Sablina, Z.A., Gureyev, A.A., Rudkovskiy, D.M., Remiz, Ye.K., NNT, "Neftepererabotka" Series, No. 1, 18 (1957).

81. Biswell, C., Catlin, W., Froming, I., Robins, C., Ind. Eng. Chem., 47, No. 18, 1998 (1955).

82. Sturgis, B.M., Tekn. ukebl., 106, No. 31, 667 (1959).

83. Ertel't, G., Perlovskiy, E., Tutuayler, T., U.S. Patent 2974025, 7 March 1961.

84. Churshukov, Ye.S., Sablina, Z.A., Shekhter, Yu.N., Englin, B.A., in collection "Proizvodstvo zhidkikh i konsistentnykh zashchitnykh smazok na moskovskom zavode "Neftegaz"" [Production of Liquid Lubricants and Greases at the "Neftegaz" Refinery at Moscow], ITEIneftegaz, 1962.

85. Shekhter, Yu.N., Goryacheva, V.I., Dol'berg, A.L., Razvadovskaya, I.N., Grishayeva, A.S., loc. cit.

86. Losikov, B.V., Smirnov, M.S., Aleksandrova, L.A., Rubinshteyn, I.A., Ochertyanyy, I.T., Dneprov, V.N., in collection "Prisadki k maslam i toplivam," Gostoptekhizdat, 1961.

87. Zul'tser, P., IV Mezhdunarodnyy neftyanoy kongress, Vol. VII, Gostoptekhizdat, 1957.

88. Lipshteyn, R.A., Khaykina, S.E., Avetisyan, A.S., Blagova, T.A., in collection "Prisadki k toplivam i maslam," Gostoptekhizdat, 1961.

89. Nikolayeva, V.G., Dukhnina, A.Ya., Komarov, B.I., Levinson, G.I., loc. cit.

90. Losikov, B.V., Fat'yanov, A.D., Mikulin, Yu.V., Aleksandrova, L.A., Koznov, G.G., Berezina, R.M., Khimiya i tekhnologiya topliv i masel, No. 8 (1961).

91. Petrol. Ref., 38, No. 6, 194 (1959).

92. Chem. Eng., 68, No. 3, 62 (1961); SAE Preprints, No. 3 (1961).

93. Englin, B.A., Rozhkov, I.V., Tugolukov, V.M., Sakodynskaya, T.P., Khimiya i tekhnologiya topliv i masel, No. 12 (1963).

94. J. Inst. Petrol., 50, No. 491, 297 (1964).

95. Oil and Gas J., 60, No. 41, 33 (1962).

96. Klinnenberg, A., Poulson, B., J. Inst. Petrol., 11, No. 44, 379, 419 (1958).

97. Kichkin, G.I., Rozhkov, I.V., Vilenkin, A.V., Kornilova, Ye.N., Khimiya i tekhnologiya topliv i masel, No. 6 (1963).

98. Sablina, Z.A., Gureyev, A.A., Nov. neft. tekhn., "Neftepererabotka" Series, No. 4, 13-14 (1955).

Manuscript Page No.	Footnotes
354	[1]Topanol O, DuPont No. 29.
360	[2]Grades with limited use.
384	[3]1 picoohm/m = 10-12 ohms/linear meter.

Manu-script Page No.	Transliterated Symbols
385	кр = kr = kriticheskiy = critical

Chapter 6

MOTOR OILS

Oil performs the following functions in internal-combustion engines:

it reduces wear of parts and prevents them from seizing;

it protects parts from the corrosive action of external agents and fuel-combustion products;

it reduces frictional losses;

it carries away the heat generated as a result of friction;

it continuously clears rubbing elements of wear products and other abrasive dirt (washes them out);

it prevents blowby of mixture (or air) and combustion products from the cylinder into the crankcase as they are compressed.

TABLE 6.1

Lubricating Systems of Automotive Engines

1 Показатели	ГАЗ-51А, ГАЗ-63 2	ЗИЛ-164 3	ЗИЛ-157	МАЗ-200 4	«Москвич» 407 и 410 5	6 М-21 «Волга»
7 Система смазки	8 Комбинированная					
9 Емкость системы, л	7,0	8,5	11,0	15,5	4,3	6,2
10 Давление масла, кГ/см²	2,0—4,5	3,0—4,0	3,0—4,0	8,0—9,0	2,0—3,5	2,0—4,0
11 Фильтрация масла	12 Двойная: фильтрами грубой и тонкой очистки					

1) Index
2) GAZ-51A, GAZ-63
3) ZIL-164
4) MAZ-200
5) "Moskvich" 407 and 410
6) "Volga" :-21
7) Lubricating system
8) Combined
9) System capacity, liters
10) Oil pressure, kg/cm²
11) Oil filtering
12) Dual: coarse and fine filters.

Most modern transport, marine and stationary internal-combustion engines use a combined lubrication system in which the bearings and certain other rubbing elements are lubricated by circu-

lating oil under pressure and the cylinder and piston by splash. Exceptions are the very smallest engines, where all elements are splash-lubricated, and low-speed, high-power stationary and marine diesels, where the bearings are lubricated by circulation under pressure and the cylinders by lubricators. The lubrication systems of certain engines are delineated in Tables 6.1-6.4.

If the oil is to perform the functions listed above, it must exhibit the following basic properties:

have a certain minimum viscosity at high temperatures and sufficient mobility at starting temperatures, so that it will perform properly throughout the entire working-temperature range;

it must be chemically stable at high temperatures under conditions of continuous contact with air and fuel combustion products, and its properties must not change during operation;

it must not corrode the material of the engine parts and must protect these parts from external corrosive agents.

TABLE 6.2

Lubricating Systems of Tractor Engines [1]

1 Показатели	2 ДТ-54	3 КДМ-46	4 Д-35 и Д-36	5 ХТЗ Б-7	6 У-1-2	7 Д-24	8 Д-14	9 ГАЗ-51	10 ЗИЛ-120
11 Система смазки	12 Комбинированная								
13 Емкость системы, л	25	27	16—17	7,4	8,5	7,8	4,5	7,0	8,5
14 Производительность насоса, л/мин	40	33,3	35	8	—	—	—	16,4	19,2
15 Давление масла, кГ/см²	1,7—2,5	1,7—2,7	2,0—3,0	1,8—2,5	1,5—30	1,8—2,2	1,8—2,1	2—4	1,5
16 Фильтрующий элемент: 17 грубой очистки	18 Металлический щелевой ленточный				—	18 Металлический щелевой ленточный	19 Полнопоточная центрифуга	20 Металлический щелевой пластинчатый	
21 тонкой очистки	22 АСФО-1 или центрифуга	23 Нитчатый хлопчатобумажный	24 АСФО-1	АСФО-3	АСФО-2	АСФР-2	25 То же	АСФО-2	АСФО-1
26 Периодичность смены картерного масла, ч	27 100—120 или 240—250 (при центрифуге)	120	100	80—100	100	180—200	240—250	1500—3100 км	

1) Index
2) DT-54
3) KDM-46
4) D-35 and D-36
5) KhTZ B-7
6) U-1-2
7) D-24
8) D-14
9) GAZ-51
10) ZIL-120
11) Lubrication system
12) Combined
13) System capacity, liters
14) Pump delivery, liters/min

15) Oil pressure, kg/cm²
16) Filtering element
17) Coarse
18) Slotted metal ribbon
19) Full-flow centrifuge
20) Slotted metal plate
21) Fine
22) ASFO-1 or centrifuge
23) Cotton filament
24) ASFO-1
25) Same
26) Crankcase oil change interval, hours
27) 100-120 or 240-250 (with centrifuge).

TABLE 6.3

Oil-System Capacities of Certain Engines with Compression Ignition

1 Марка двигателя	2 Мощность, л. с.	3 Оборотность, об/мин	4 Емкость масляной системы, л	1 Марка двигателя	2 Мощность, л. с.	3 Оборотность, об/мин	4 Емкость масляной системы, л
5 Двухтактные				9 Четырех-			
6 1-2Д 16/20	15—30	650	20—40*	10 тактные			
1-2Д 16/27	25—50	430	20—40	1-6Ч 10, 5/13	10—60	1500	5—25
1-2Д 16, 5/20	20—50	750	20—40	1Ч 12/16	13	1200	5
2-6Д 19/32	70—210	430	40—100	2-4Ч 8, 5/11	10—20	1500	6—10
				2-4Ч 13/18	40—80	1500	18—26
2Д 20/30	50	430	50	4-8Ч 16, 5/21	130—250	1300	80—160
4Д 24/36	240	375	100				
4-8Д 30/50	400—800	300	400—800	6Ч 12/14	80	1500	25
				6-12Ч 15/18	150—300	1500	50—75
7 8ДР 43/61	2000	250	800				
8 2-4ДСП 19/30	80—160	500	40—60	6-8Ч 23/30	450—600	1000	200—270
				6Ч 36, 5/45	600	375	370
				12Ч 18/20	700	1500	75

*The extreme engine-power values and the oil-system capacities for the minimum and maximum number of cylinders of the given type of engine are indicated.

1) Engine type
2) Power, hp
3) Rated speed, rev/min
4) Oil system capacity, liters
5) Two-cycle
6) 1-2D 16/20
7) 8DR 43/61
8) 2-4DSP 19/30
9) Four-cycle
10) 1-6Ch 10, 5/13.

TABLE 6.4

Typical Lubrication System of Piston Aviation Engine [2]

1 Характеристика	2 Показатель
3 Система смазки	4 Циркуляционная комбинированная с сухим картером
5 Заправочная емкость масляного бака, л	60
6 Применяемое масло	7 МС-22 или МС-20
8 Удельный расход масла на эксплуатационном режиме, г/(л. с. ч.)	12
9 Давление масла в системе, $кГ/см^2$	0,8—16
10 Температура масла:	
11 на входе в двигатель	50—85
12 на выходе из двигателя	115—125
13 Масляные насосы	14 Шестеренчатые
15 Фильтры	16 Пластинчатые
17 Перепад давления на фильтре, $кГ/см^2$	0,2—3,0

1) Characteristic
2) Index
3) Lubrication system
4) Combined circulation with dry sump
5) Oil tank filling capacity, liters
6) Oil used
7) MS-22 or MS-20
8) Specific oil consumption at rated speed, g/(hp-h)
9) Oil pressure in system, kg/cm^2
10) Oil temperature
11) At entry into engine
12) At exit from engine
13) Oil pumps
14) Gear
15) Filters
16) Plate
17) Pressure drop across filter, kg/cm^2.

Motor oils are classified into the following groups on the basis of intended use:

automotive – for lubrication of the parts of carburetor automotive engines;

aviation – for lubrication of the parts of piston-type aviation engines, whether with carburetors or fuel injection;

diesel – for lubrication of engines with compression ignition (automotive, tractor, locomotive, marine, stationary, etc).

Specific requirements are made as to the quality of each of the oils listed above, and they are appropriately reflected in the technical specifications for oils for a given application. However, even in their present-day form, ordinary oil technical specifications do not exhaustively characterize all properties of the oils, but are better adapted for technological control in the pro-

TABLE 6.5

Classification of Motor Oils [3]

1 Показатели	2 Группы масел и их индексация						9 Соответствие масла по советской классификации маслу по классификации SAE
	3 А (типа Премиум)	4 Б (типа Хеви-Дьюти)	5 В (типа Серии 1)	6 Г (типа Серии 2)	7 Д (типа Серии 3)	8 Е (типа Мобильгард 593)	
10 Вязкость при 100° С, *ccm*							
6,0 ± 0,5	М-6А	11 М-6Б	12 М-6В	—	—	—	SAE-20
8,0 ± 0,5	М-8А	М-8Б	М-8В	13 М-8Г	14 М-8Д	—	SAE-20
10,0 ± 0,5	М-10А	М-10Б	М-10В	М-10Г	М-10Д	—	SAE-30
12,0 ± 0,5	М-12А	М-12Б	М-12В	М-12Г	М-12Д	—	SAE-30
14,0 ± 0,5	М-14А	М-14Б	М-14В	М-14Г	М-14Д	—	SAE-40
16,0 ± 0,5	М-16А	М-16Б	М-16В	М-16Г	М-16Д	15 М-16Е	SAE-40
20,0 ± 0,5	М-20А	М-20Б	М-20В	М-20Г	М-20Д	М-20Е	SAE-50
16 Отечественные методы и двигатели, временно рекомендуемые для установления серии масла	Газ-51, 100 ч 17	Газ-51, 100 ч; 18 Д-54 или Д-38, 480 ч; НАТИ-УИМ-6, 120 ч	19 Д-54, или Д-38, 480 ч; НАТИ-УИМ-6, 120 ч	ЯАЗ-204, 20 550 ч	ЯАЗ-204, 20 550 ч	ДК-2 (дизель-компрессор) на моторном топливе 21 с содержанием серы 1,5%, 36 ч	—
22 Зарубежные установки	23 Петтер W = 1		24 Катерпиллер			—	—
25 Зарубежные методы испытаний	26 Петтер W = 1, 36 ч (брит. станд. IP176/64)	27 1А, 480 ч (брит. станд. 124/64; станд. США 332T)	28 1А, 480 ч (спецификации британской армии DEF 2101B и спецификации флота США MIL-L-9000A)	29 1D, 480 ч (брит. станд. 173/60; станд. США 340T)	30 1G, 480 ч (станд. США 341-T) и 1Д, 480 ч (брит. станд. 173/60; станд. США 340T)	31 Нестандартные методы на двигателях типа Bolnes, Ruston Hornsby и др. с лубрикаторной системой смазки	—
32 Топливо	33 Бензин	34 Дизельное малосернистое	35 Дизельное сернистое		36 1D — дизельное сернистое 1G — дизельное малосернистое	—	—
37 Назначение масла	38 Для автомобильных карбюраторных двигателей, авиационных поршневых двигателей и дизелей, работающих на малосернистом топливе	39 Для форсированных автомобильных карбюраторных двигателей и тракторных дизелей, работающих на малосернистом топливе	40 Для форсированных автомобильных карбюраторных двигателей и дизелей всех назначений, работающих на сернистом топливе	41 Для форсированных дизелей всех назначений, работающих на сернистом топливе	42 Для высокофорсированных дизелей всех назначений	43 Для тихоходных судовых дизелей с лубрикаторной цилиндровой системой смазки и СПГГ (свободных поршневых генераторов газа), работающих на тяжелых сернистых топливах	—
44 Масло, по классификации API (Амер. нефт. ин-т)	MM	MS-DG	MS-DM	DS	DS	—	

Note. Motor oils without additives or only with a depressor (Regular type) are not included in the new classification as being without further interest.

1) Index
2) Oil group and indexing
3) A (Premium type)
4) B (Heavy Duty type)
5) V (Series 1 type)
6) G (Series 2 type)
7) D (Series 3 type)
8) Ye (Mobilgard 593 type)
9) SAE oils corresponding to Soviet class
10) Viscosity at 100°C, cSt
11) M-6B
12) M-6V
13) M-8G
14) M-8D
15) M-16Ye
16) Soviet methods and engines recommended provisionally for establishment of oil series
17) Gaz-51, 100 h
18) Gaz-51, 100 h; D-54 or D-38, 480 h; NATI-UIM-6, 120 h
19) D-54 or D-38, 480 h; NATI-UIM-6, 120 h
20) YaAZ-204, 550 h
21) DK-2 (diesel-compressor) on motor fuel containing 1.5% sulfur, 36 hr
22) Foreign test machines
23) Pitter W = 1
24) Caterpillar
25) Foreign test methods
26) Pitter W = 1, 36 h (British standard IP176/64)
27) 1A, 480 h (British standard 124/64; American standard 332T)
28) 1A, 480 h (British army specifications DEF 2101B and U.S. Navy Specification MIL-L-9000A)
29) 1D, 480 h (British standard 173/60; American standard 340T)
30) 1G, 480 h (American standard 341-T) and 1D, 480 h (British standard 173/60; American standard 340T)
31) Unstandardized methods on Bolnes, Ruston, Hornsby and other engine types with lubricator lubrication
32) Fuel
33) Gasoline
34) Low-sulfur diesel
35) Sulfur-containing diesel
36) ID – sulfur-containing diesel; IG – low-sulfur diesel
37) Application of oil
38) For carburetor automotive engines, piston-type aviation engines and diesels operating on low-sulfur fuel
39) For tuned carburetor-type automotive engines and tractor diesels operating on low-sulfur fuel
40) For tuned carburetor-type automotive engines and all diesel applications using sulfur-containing fuel
41) For tuned diesels in all applications using sulfur-containing fuel
42) For highly tuned diesels, all applications
43) For slow marine diesels with lubricator system for cylinders and FPGG (СПГГ) (free piston gas generators) operating on heavy sulfur-containing fuels
44) Oil according to API (American Petroleum Institute) classification.

duction process. Only in recent years have indices characterizing the operational properties of the oils to one or another degree made their appearance in technical specifications for oils. These indices include stability to thermal oxidation, detergency, corrosiveness, and certain others. Tests on full-scale and model machines are acquiring increasing significance in evaluation of oil properties. The results of these oil tests, together with the most important physicochemical indices, form the basis for contemporary Soviet and foreign oil classifications.

1. SOVIET MOTOR-OIL CLASSIFICATION

The prevailing grouping of oils by production methods and basic applications, without consideration of their operational properties, is unsatisfactory from the standpoint of engine manufacturers and users, for whom the operational qualities of the oil as applied to an engine with a given degree of tuning with consideration of the characteristics of the fuels used in that engine are of prime importance.

Accordingly (Table 6.5), it has been proposed that motor oils be divided into 7 viscosity groups; oils M-6 and M-8 are winter grades for automobiles and tractors; all other oils from M-10 to M-20 are used during the summer and winter, depending on temperature conditions and the environment of the machine or engine (open air, indoors, ship, etc.).

Depending on the type of engine, its degree of tuning, its thermal and mechanical stressing, and the type and properties of its fuel, it has been proposed that oils be classified into 6 groups: A, B, V, G, D and Ye, to correspond to the prevailing foreign classification. Table 6.5 indicates the correspondence of the oil groups to the foreign viscosity (SAE) and property or application (API) classifications.

For an oil to be assigned to a group (series), it must pass the appropriate engine test, followed by comparison with a reference standard. Each type (grade) of motor oil has a code designation, e.g., M-6A stands for motor oil, viscosity 6 cst at 100°C, group A (Premium); M-20D is a motor oil with a viscosity of 20 cst at 100°C, group D (Series 3), and so forth [4].

2. FOREIGN MOTOR-OIL CLASSIFICATIONS

The basic classification in use in all foreign countries for motor and transmission oils for various purposes is the SAE (Society of Automotive Engineers) classification, in which each oil is designated by number in accordance with its viscosity. The viscosity is determined at 0°F (-17.7°C) for winter-grade oils, which are coded with the letter "W" (Winter) in the classification in addition to the number, or at 210°F (98.9°C) for all other oils. In 1950, the SAE classification was supplemented by the multigrade oils, which have a double numerical designation: the first number symbol characterizes the viscosity of the oil at subfreezing temperatures and the second at above-freezing temperatures.

Table 6.6 lists oil viscosities according to the SAE classi-

TABLE 6.6

Classification of Oils by SAE Numbers

1 № SAE	2 Вязкость (в сст) при −17,8° С		2 Вязкость (в сст) при +98,9° С	
	3 минимум	4 максимум	3 минимум	4 максимум
5W	—	880	—	—
10W	1300	2 600	4,2	—
20W	2600	10 050	5,75	—
20	—	—	5,75	9,7
30	—	—	9,7	13,0
40	—	—	13,0	16,85
50	—	—	16,85	22,75

1) SAE No.
2) Viscosity (cSt) at ...°C
3) Minimum
4) Maximum.

TABLE 6.7

Viscosities of Multigrade Oils

1 Марка	2 Вязкость, сст		5 Минимальный индекс вязкости
	3 максимальная при −17,8° С, экстраполированная по кривым ASTM	4 минимальная при 98,9° С	
5W-10	870	4,2	90
5W-20	870	6,0	140
5W-30	870	6,5	154
5W-40	870	13,0	156
5W-50	870	16,8	156
10W-20	2600	6,0	90
10W-30	2 600	6,5	132
10W-40	2 600	13,0	139
10W-50	2 600	16,8	144
20W-30	10 050	6,5	97
20W-40	10 050	13,0	113
20W-50	10 050	16,8	120

1) No.
2) Viscosity, cSt
3) Maximum at -17.8°C, extrapolated in accordance with ASTM curves
4) Minimum at 98.9°C
5) Minimum viscosity index.

fication, and Table 6.7 presents the supplement to this classification for multiviscosity oils. The SAE classification does not set standards for such indices of oils as their oxidation stability and other indices that characterize the use properties of the oils. The upper and lower oil-viscosity values permitted by the classification are rather widely separated for each grade. Requirements based on tests of the oils in special engines are formulated in specifications that take the operating conditions of the oil into consideration.

The first group, the so-called regular-grade oils, includes

oils without additives that are suitable for use in lightly stressed automotive engines. The second group is composed of oils of the better "Premium" grade, which contain additives that improve their antiwear properties and antioxidants. The third group embraces oils for severe operating conditions (heavy duty, HD), which contain additives that endow the oils with detergent properties, i.e., the ability to prevent formation of varnishes and carbon deposits on hot engine parts, and prevent piston-ring burning. Usually, anticorrosion additives are also used in these oils to prevent corrosion of bearings made from easily corroded alloys.

Oils meeting specifications MIL-L-2104A and DEF-2101B were used until recently.

In 1962-1963, the new motor-oil specification MIL-L-2104B was introduced; it differs from MIL-L-2104A, which was adopted in 1954, in having requirements for evaluation of the oil's tendency to form sludge and its corrosive aggressiveness during cold engine operation [5-7].

In connection with the extensive use of diesel fuels with high (up to 1%) sulfur contents, it became necessary to develop oils that possess higher detergent properties. Special oil grades were created for very heavy duty conditions — Supplement I and Supplement II or Series 2. Over the last few years, the Caterpillar Tractor Co. developed specifications for Series 3 oils. These oils contain a large quantity of highly efficient detergent additives (15-20%) and can be used in the most highly stressed diesel engines in operation on high-sulfur fuels. In the U.S. Army, Specification MIL-L-45199 provides a Series 3 oil quality.

The American Petroleum Institute (API) has proposed a letter system for indicating oil use conditions.

ML: gasoline engines with spark ignition, without design features that might cause formation of sludge, and not imposing any special requirements on the oil.

MM: gasoline engines for medium and heavy duty conditions that tend to promote formation of sludge and bearing corrosion, and having high crankcase-oil temperatures.

MS: gasoline engines operating under unfavorable conditions, in which special requirements must be made of the oil as regards freedom from sludge formation and bearing corrosion because of engine design features or fuel properties.

DG: diesels that impose no particularly rigid requirements on the oil (wear and corrosion of parts or formation of deposits on them).

DM: diesels operating under heavy-duty conditions or using ordinary fuel but not having design or operational peculiarities that make them particularly sensitive to solid deposits forming from the oil.

DS: diesels operating under exceptionally heavy-duty condi-

tions that promote formation of deposits and accelerated wear for reasons related to the design of the engine or fuel properties.

In recent years, in connection with the development of high-powered V-type automotive engines, the API specification for class MS oils has been supplemented by a series of requirements relating to tests of these oils on a number of highly tuned automotive engines. These requirements are also reflected in the American specifications (ASTM G-IV-MS).

Continental European specifications basically duplicate the American and British specifications MIL-L-2104A and DEF-2101B.

3. MOTOR METHODS FOR EVALUATION OF OIL QUALITY

The operational properties of oils for internal-combustion engines are determined on single-cylinder or multicylinder engines in accordance with a strictly regulated program and on a specific grade of fuel (Tables 6.8 and 6.9). Tests on the UIM-1 machine have the purpose of establishing the tendency of the oil to cause piston-ring burns and form deposits on the piston. The amount of the deposits and their nature are determined. The test method using the UIM-6 machine is recommended for evaluation of group V oil quality (see Table 6.5). The results of determination of the mobility of the rings, the amount of deposits on the pistons and rings are evaluated by a point system; sleeve wear is evaluated by the crescent-cut method, ring wear by direct weighing, and over-all wear by the amount of iron in the oil.

The OD-9 engine is used (by method I) to evaluate the tendency of oils with additives to form varnish deposits on the piston, determining them according to AUSS 5726-53. Also determined is the amount of deposits on the piston, rings and special "witnesses" inserted in the piston. The same engine is used in method II to characterize the detergent action of the additives and the oxidation stability of oils with additives.

Tests on the IT9-2 are run to determine the varnishing capacity of automotive oils with additives, a quantity determined by AUSS 5726-53. In tests on the IT9-3, which have the purpose of determining the tendency of diesel oils to form deposits, the rating parameter is the sum of indices for deposits and piston-ring mobility. The IT9-5 machine is used to evaluate corrosive aggressiveness and detergency of automotive oils.

The GAZ-51 engine is used to evaluate the tendency of an oil to form sludge at the bottom of the crankcase and in the valve chamber of the engine (see Table 6.9). A 100-h test is also run on the GAZ-51 engine for general evaluation of oil quality in groups A and V (see Table 6.5). Tests are run on the D-54 or D-38 engine for general evaluation of diesel-oil quality in groups B and V of the Soviet classification. Piston-ring mobility, deposits on the piston, over-all fouling of the engine, filter deposits, oxidation of the oil, and cylinder and piston-ring wear are evaluated in this test. The YaAZ-204 two-stroke diesel is used to evaluate the quality of group G and D oils. In addition to the parameters listed above, corrosion of bearing antifriction alloys is also evaluated in these tests.

TABLE 6.8

Soviet Metnods for Rating Oils on Single-Cylinder Engines

1 Характиристика двигателя и условия испытания	2 УИМ-1	2 УИМ-3	3 ОД-9 I	3 ОД-9 II	4 ИТ9-2	4 ИТ9-3	4 ИТ9-5
5 Тип двигателя	6 Цилиндр Д-54	7 Цилиндр Д-75	3 ОД-9	ОД-9	4 ИТ9-2	ИТ9-3	ИТ9-5
8 Рабочий объем, л	—	1,86	3,18	3,18	0,65	—	0,65
9 Диаметр цилиндра, мм	125	125	150	150	85	—	85
10 Ход поршня, мм	—	152	180	180	115	—	115
11 Продолжительность работы, ч	45	120	10	90 (3×30)	5—25	10	20
12 Число оборотов в минуту	1300	1500	1800	1300	1200	1200	1200
13 Мощность, л. с.	12,5	21	34—35	60	—	—	—
14 Расход топлива, кг/ч	2,6	4,4—4,5	—	—	0,97	0,96	1,3
15 Температура, °C:							
16 охлаждающей жидкости	135	115	140	135—140	180	150	200
17 масла	100	95	100—105	135	100	85	100
18 Количество масла в картере, кг	19 8,7 л	5	15	60	2	2	2
20 Топливо	21 Дизельное (ГОСТ 305—62)		21 Дизельное (ГОСТ 4749—49)	(ГОСТ 305—62)	Бензин Б-70 22	21 Дизельное (ГОСТ 4749—49)	Бензин Б-70 22
23 Сера в топливе, %	1,0	—	24 До 0,2	0,5—0,6	—	До 24 0,2	—
25 Давление наддува, кГ/см²	—	—	—	1,3	—	—	—

1) Characteristics of engine and test conditions
2) UIM-...
3) OD-9
4) IT9-...
5) Engine type
6) D-54 cylinder
7) D-75 cylinder
8) Displacement, liters
9) Bore, mm
10) Stroke, mm
11) Running time, h
12) Revolutions per minute
13) Power, hp
14) Fuel consumption, kg/h
15) Temperatures, °C
16) Coolant
17) Oil
18) Amount of oil in crank-case, kg
19) 8.7 liters
20) Fuel
21) Diesel (AUSS ...)
22) B-70 gasoline
23) Sulfur in fuel, %
24) Less than
25) Boost pressure, kg/cm².

TABLE 6.9

Soviet Methods of Rating Oils on Multicylinder Engines

Характеристика двигателя и условия испытания 1	ГАЗ-51 2	Д-35 3	Д-38 4	ЯАЗ-204 5	Д-54 6
	2	3	4	5	6
7 Тип двигателя	ГАЗ-51	Д-35	Д-38	ЯАЗ-204	Д-54
8 Число цилиндров . . .	6	4	4	4	4
9 Диаметр цилиндра, мм	82	100	105	108	125
10 Ход поршня, мм . . .	110	130	130	127	—
11 Продолжительность работы, ч	24	100	100	140 и 12 550	480
13 Мощность, л. с.	14 Переменная	—	—	—	—
15 Число оборотов в минуту	16 То же	1420	1420	—	—
17 Среднее эффективное давление, кГ/см² . .	—	5,5	5,6	—	—
18 Температура, °C:					
19 охлаждающей жидкости	35—40	95	95	—	—
20 масла	35—40	92	92	—	—
21 Количество масла в картере, л	6	12,3	12,8	—	—
22 Топливо	23 Бензин	Дизельное 24	—	24 Дизельное	
25 Сера в топливе, % . .	—	1,0	1,0	1,0	1,0

1) Characteristics of engine and test conditions
2) GAZ-51
3) D-35
4) D-38
5) YaAZ-204
6) D-54
7) Engine type
8) Number of cylinders
9) Bore, mm
10) Stroke, mm
11) Running time, hours
12) And
13) Power, hp
14) Variable
15) Revolutions per minute
16) Same
17) Average effective pressure, kg/cm²
18) Temperatures, °C
19) Coolant
20) Oil
21) Amount of oil in crankcase, liters
22) Fuel
23) Gasoline
24) Diesel
25) Sulfur in fuel, %.

TABLE 6.10

Specification Methods Used Abroad for Rating Oils on Single-Cylinder Engines

1 Характеристика двигателя и условия испытания	2 Питтер W-1	2 Питтер AV-1	3 Катерпиллер IA (L-1)	3 Катерпиллер IB	3 Катерпиллер ID	3 Катерпиллер IG	L-38	LTD
4 Оцениваемое масло	5 Премиум, ХД, Сапплемент I	6 ХД, Сапплемент I	6 ХД, Сапплемент I	7 Сапплемент I, ВМФ США	8 Серия 2, 3	8 Серия 3	9 ХД, Серия 3	10 Спецификация MIL-L-2104B
11 Тип двигателя	2 Питтер W-1	2 Питтер AV-1	3 Катерпиллер				12 Лабеко (CLR)	
13 Рабочий объем, л	0,47	0,553	3,40	3,40	3,40	2,0	0,7	
14 Диаметр цилиндра, мм	85	80	146	146	146	130	98	
15 Ход поршня, мм	82,5	110	203	203	203	165	95	
16 Число оборотов в минуту	1500	1500	1000	1000	1200	1800	3150	18 1800
17 Мощность, л. с.	3,3	5,0	20	20	42,5	43	5	18 Переменная
19 Продолжительность работы на режиме, ч	21 36	120	480	480	480	480	40	180
20 Расход топлива	20 мл за 45,2 сек	1,08 кг/ч 22	735±15 ккал/мин 23	743 ккал/мин	1600±15 ккал/мин	1474 ккал/мин	2,0—2,25 кг/ч 22	—
24 Среднее эффективное давление, кГ/см²	4,2	5,3	5,3	5,3	9,5	9,0	—	—
25 Температура, °С:								
26 охлаждения жидкости	150	85	82	54	93	88	93	18 Переменная
27 масла	138	55	65	63	79,5	96	138	Не регламентируется 28
29 воздуха на всасывании	28 Не регламентируется		30 Не более 32	30 Не более 32	93	124	31 27 (минимум)	—
32 Объем масла в картере, л	1,14	3,7	5,7	5,7	5,7	5,7	1,65	1,2
33 Срок смены масла, ч	34 Без смены		120	120	120	120	34 Без смены	
35 Давление наддува, кГ/см²	—	—	—	—	1,48	1,77	—	—
36 Топливо	Бензин 37	38 Дизельное					39 Изооктан+0,8 мл ТЭС на 1 л	ВМР-215—59
40 Сера, %	0,1—0,25	0,35—0,45%, метод А 41; 0,95—1,05%, метод Б 41	0,35—0,4 42 (ХД); 1,0±0,05 (Сапплемент I) 43	44 Не менее 0,8	1,0±0,05	0,35—0,45	—	—

1) Characteristics of engine and test conditions
2) Pitter
3) Caterpillar
4) Oils rated
5) Premium, HD, Supplement I
6) HD, Supplement I
7) Supplement I, U.S. Navy
8) Series ...
9) HD, Series 3
10) Specification MIL-L-2104B
11) Engine type
12) Lubeco
13) Displacement, liters
14) Bore, mm
15) Stroke, mm
16) Revolutions per minute
17) Power, hp
18) Variable
19) Running time at conditions, hours
20) Fuel consumption
21) 20 ml in 45.2 s
22) 1.08 kg/h
23) ... kcal/min
24) Average effective pressure, kg/cm²
25) Temperatures, °C
26) Coolant
27) Oil
28) Not regulated
29) Air at induction
30) Not above
31) Minimum
32) Volume of oil in crankcase, liters
33) Oil change interval, h
34) No changes
35) Boost pressure, kg/cm²
36) Fuel
37) Gasoline
38) Diesel
39) Isooctane + 0.8 ml of TEL to 1 liter
40) Sulfur, %
41) Method
42) (HD)
43) (Supplement I)
44) No less than.

The DK-2 diesel compressor is used to rate oils intended for slow-running diesels with a separate (lubricator) oiling system.

The characteristics of single-cylinder diesels used abroad to evaluate oil quality are given in Table 6.10. This table also indicates test conditions.

TABLE 6.11

American Specification Methods for Rating Oils on Multicylinder Engines

1 Характеристика двигателя и условия испытания	L-4 (CRC-L-4-545)	GM-71 2 спецификации			
		MIL-L-9000B	MIL-P-17 269	MIL-P-17 276	MIL-P-17 273
3 Тип двигателя	4 Шевроле	5 Дженерал Моторс, тип 3-71C			
6 Число цилиндров	6	3			
7 Рабочий объем, л	3,54	3,3			
8 Диаметр цилиндра, мм	88,9	108			
9 Ход поршня, мм	95,2	127			
10 Мощность, л. с.	30	84	84	84	45
11 Число оборотов в минуту	3150±25	1800	1800	1800	1200
12 Продолжительность работы, ч 13	36	300	300	100	300
Температура, °C:					
14 охлаждающей жидкости	93	93,5	94	77	80
15 масла	17 138	121	110	94	107
16 Топливо	Бензин	18 Газойль			
19 Сера, %	—	0,95—1,05	0,8	0,8	0,3—0,4

1) Characteristics of engine and test conditions
2) Specification
3) Engine type
4) Chevrolet
5) General Motors type 3-71C
6) Number of cylinders
7) Displacement, liters
8) Bore, mm
9) Stroke, mm
10) Power, hp
11) Revolutions per minute
12) Running time, h
13) Temperatures, °C
14) Coolant
15) Oil
16) Fuel
17) Gasoline
18) Gas oil
19) Sulfur, %.

The Caterpillar L-1 or 1A method is used on a Caterpillar engine for comprehensive rating of Heavy-Duty-type oils that meet Specifications DEF-2101B and MIL-L-2104A and Supplement 1 (Series 1) oils.

Caterpillar method IE is used to rate oils used by the U.S. Navy (MIL-L-9000A), Caterpillar method 1D for Series 2 and 3 oils, and Caterpillar method 1G for oils of Series 3 only. Testing of Series 3 oils on the Caterpillar 1D and 1G engines is provided by the USA's Specification MIL-L-45199.

The Pitter W-1 and AV-1 methods were developed in England. The Pitter W-1 method permit evaluation of the oxidation stability of motor oils, their corrosive aggressiveness, and their ten-

TABLE 6.12

Conditions of Classification Tests Provided by ASTM List GIV-MS

1 Показатели	2 Двигатель Олдсмобиль 1958—60 A	3 Б	4 В	5 Двигатель Десото 1958	6 Двигатель Линкольн-Меркури 1957 7 1 режим	8 2 режим	9 3 режим
10 Число оборотов в минуту	2500±20	1500±20	3600±20	3600	500	2500	2500
11 Мощность, л. с.	2	25±2	85±2	0	0	105	105
12 Температура воды, °C:							
13 на выходе из двигателя	35±1	35±1 15	93±1 15	82	47	52	77
14 на входе в двигатель	29 (миним.) 15	29 (миним.)	80 (миним.)	—	—	—	—
16 Температура масла, °C	49 (макс.) 17	49±1	120±1	105	52	82	99
18 Отношение воздух : топливо	—	16 : 1	16 : 1	—	9,5 : 1	15,5 : 1	15,5 : 1
19 Затяжка пружины клапана	20 Нормальная			136% от максимальной 21	20 Нормальная		
22 Расход масла, л	23 5 (на все три испытания)			—	24 Не более 7,5 (на все испытания)		
25 Работа двигателя	10 мин 26	3 ч 27	40 ч 27	2 ч 27	45 мин	2 ч	75 мин 26
28 Остановка двигателя	50 мин	3 ч	—	2 ч	— 26	— 27	—
29 Число этапов (циклов)	80	10	1	6	48	48	48
30 Общая продолжительность испытания, ч	80	60	40	24	—	192	—
31 Топливо	32 Бензин с 0,8 мл ТЭС на 1 л			Не регламентируется 33	34 Обычное зимнее		
	35 Содержание серы 0,16±0,02 вес. %						
36 Вентиляция картера	37 Заглушена		36 Нормальная	—	—	—	—
39 Оцениваемые показатели	Точечная коррозия и следы задира на толкателях клапанов и кулачковом вале 40	Интенсивность ржавления 41	Коррозия, лаковые отложения и осадки 42	Противозадирные свойства 43	Образование низкотемпературных осадков 44		

1) Index
2) 1958-60 Oldsmobile engine
3) B
4) C
5) 1958 DeSoto engine
6) 1957 Lincoln-Mercury engine
7) Test No. 1
8) Test No. 2
9) Test No. 3
10) Revolutions per minute
11) Power, hp
12) Water temperature, °C
13) Leaving engine
14) Entering engine
15) Minimum
16) Oil temperature, °C
17) Maximum
18) Air:fuel ratio
19) Valve-spring tensioning
20) Normal
21) 136% of maximum
22) Oil consumption, liters
23) 5 (in all three tests)
24) No more than 7.5 (in all tests)
25) Engine running time
26) Minutes
27) Hours
28) Engine-off time
29) Number of steps (cycles)
30) Total test time, hours
31) Fuel
32) Gasoline with 0.8 ml of TEL per 1 liter
33) Not regulated
34) Normal winter
35) Sulfur content 0.16 ± 0.02% by mass
36) Crankcase ventilation
37) Plugged
38) Normal
39) Indices evaluated
40) Pitting corrosion and traces of scoring on valve pushrods and camshaft
41) Rate of rusting
42) Corrosion, varnish deposits, and sludge
43) Antiscoring properties
44) Formation of low-temperature sludge.

dency to form varnish deposits. The Pitter AV-1 method is designed to characterize the detergent properties of diesel oils.

The L-38 method used with the Lubeco engine is used to determine the oxidizabilities of oils and their corrosion properties. At the present time, this method is replacing the Chevrolet (L-4) test, which had been used to characterize the qualities of oils with various series of additives (Table 6.11). Testing on the Lubeco engine by the LTD method makes it possible to evaluate the tendency of oils to low-temperature sludge formation (MIL-L-2104B).

The detergent properties of oils meeting the requirements of the same specification are evaluated by Caterpillar method I-H.

The GMC Type 3-71C two-stroke engine is extensively used to rate oils conforming to Specifications MIL-L-9000A and MIL-L-9000E, which apply in the U.S. Navy. Tests of the series run on this engine differ in conditions, duration, and type of fuel used, and yield a comprehensive evaluation for oils to be used in Navy powerplants. From 1 to 2% of sea water is added to the oil periodically to bring the test conditions closer to those of actual use.

A series of tests on 1958-1960 Oldsmobile, 1958 DeSoto, and 1957 Lincoln engines has been adopted for evaluation of the suitability of class MS oils for use in modern high-powered V-type automotive gasoline engines in accordance with ASTM List GIV-MS.

Tests on a 1958-1960 Oldsmobile engine fitted with a special carburetor and two copper-lead connecting-rod bearings are run in three successive (no oil change) stages (A, B, C), as shown in Table 6.12, by the GMC method with the purpose of rating the oil under high- and low-temperature operating conditions.

The test on the DeSoto engine permits evaluation of the properties of the oil in high-temperature operation; the test with the Lincoln engine rates them at low temperatures (see Table 6.12).

4. VISCOSITY AND VISCOSITY-TEMPERATURE PROPERTIES OF MOTOR OILS

For most engines, the required oil-viscosity levels (in cst at 100°C) lie within the following ranges:

Carburetor automotive engines	6-10
Diesels, all applications	8-16
Piston-type aviation engines (carburetor and fuel injection)	18-24

During the cold season of the year and in regions with low air temperatures, oils with lower viscosities are used in automotive engines and diesels.

The viscosities of commercial grades of automotive, diesel and aviation oils are given in Table 6.13.

Knowledge of the viscosity at one or two temperatures is usually insufficient for comprehensive evaluation of oil viscosity properties. The viscosity properties of oils are characterized

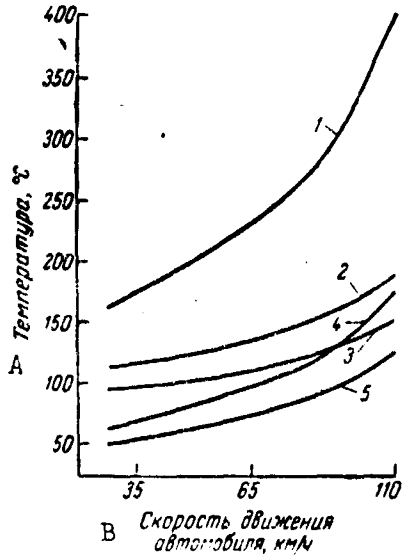


Fig. 6.1. Influence of load on automotive engine on average temperature of parts and lubricating oil: 1) middle of top of piston; 2) cylinder wall (top); 3) cylinder wall (bottom); 4) crankshaft bearings; 5) oil in crankcase. A) Temperature, °C; B) speed of vehicle, km/h.

TABLE 6.13

Basic Quality Indices of Oils Used to Lubricate Internal-Combustion Engines

1 Показатели	2 Авиационное масло				4 Специальное масло		5 Дизельное масло							7 Моторное масло	
	3 ГОСТ 1013—49			ГОСТ 9320—60	ГОСТ 6360—58		ГОСТ 5304—54				ГОСТ 8581—57	ВТУ НП 23—58	6 ВТУ НП 80—60	ГОСТ 1862—63	8 ВТУ 22—58
	МК-22	9 МС-20	9 МС-14	10 МС-20С	11 МТ-16п	11 МТ-14п	12 Дп-14	12 Дп-11	13 Д-11	12 Дп-8	14 ДСп-11	14 ДСп-8	15 М-12В	16 без присадки	17 с присадкой ЦИАТИМ-339
19 Вязкость кинематическая, *сст*: при 100° C	19 Не менее 22	19 Не менее 20	19 Не менее 14	19 Не менее 20	16,0—17,5	13,5—14,5	13,5—15,5	10,5—12,5	10,5—12,5	8—9	10,5—11,5	8,2—8,5	12	62—68 (при 50° C) 20	
21 Отношение кинематической вязкости при 50° C к кинематической вязкости при 100° C, не более	8,75	7,35	6,65	7,6	7	4	7,75	6,5	7,3	6,0	6,0	5,5	6,2	—	—
22 Зольность, %:															
23 для масла без присадки, не более	0,004	0,003	0,003	0,003	—	—	—	—	0,005	—	—	0,01	0,005	0,04	0,04
24 для масла с присадкой ЦИАТИМ-339, не менее	—	—	—	—	0,25	0,13	0,25	0,25	—	0,25	0,25	0,3	0,3 (с 1% присадки 25 ВНИИ НП-360)	0,4	0,4
26 Коксуемость до добавления присадки, %, не более	0,7	0,3	0,45	0,45	0,30	0,20	0,55	0,4	0,4	0,2	0,3	0,15	—	0,4	0,4
27 Кислотное число, *мг* KOH на 1 *г*, не более:															
28 без присадки	0,1	0,05	0,25	0,05	—	—	—	—	0,15	—	—	0,02	0,02	—	—
29 с присадкой	—	—	—	—	0,15	0,10	0,10	0,10	—	0,10	0,02	—	—	—	—
30 Температура застывания, °C, не выше	—14	—18	—30	—18	—25	—43	—10	—15	—18	—25	—15	—25	—15	0	—
31 Термоокислительная стабильность по методу Папок при 250° C, *мин*, не менее	35	17	20	17	—	25	25	20	—	20	—	—	—	—	—
32 Коррозия (испытание на пластинках из свинца марки C1 или C2), *г/м²*, не более	20	45	00	15	10	10	13	13	—	13	10	10	10	—	—

TABLE 6.13 (continued)

[1] Показатели	[33] Масла автомобильные с присадкой; [3] ГОСТ 5303—50				[34] Масла автомобильные специальные; ГОСТ 3829—51		[35] Масла автотракторные; ГОСТ 1862—60					
	[36] АСп-5	[37] АКп-5	[36] АСп-9,5	[37] АКп-9,5	[38] летнее	[39] зимнее	[40] АКЗп-6	[36] АСп-6	[41] АКЗп-10	[37] АКп-10	[36] АСп-10	АК-15
[42] Вязкость кинематическая, *сст*:												
[43] при 100° С	[19] Не менее 5	5	9,5	9,5	45—60 (при 50° С) [25]	29—33 (при 50° С) [25]	[19] Не менее 6,0	6,0	10,0	10,0	10,0	15,0
[44] » 0° С, не более	—	—	—	—	—	—	600	1500	1000	—	—	—
[45] Отношение кинематической вязкости при 50° С к кинематической вязкости при 100° С, не более	7,0	8,6	7,4	8,8	—	—	4,0	5,5	4,5	7,0	6,8	9,0
[46] Зольность, %:												
[47] для масла без присадки, не более	—	—	—	—	—	—	0,010	0,010	0,010	0,015	0,010	0,015
[48] для масла с присадкой ЦИАТИМ-339, не менее	—	—	—	—	[49] С 3% присадки НАКС, не более 0,2	0,2	0,26	0,26	0,26	0,26	0,26	—
[50] Коксуемость до добавления присадки, %, не более	—	—	—	—	[51] С 3% присадки НАКС, 0,8	0,8	0,10	0,10	0,15	0,40	0,25	0,70
[52] Кислотное число, *мг* КОН на 1 *г*, не более:												
[53] без присадки	—	—	—	—	—	—	0,10	0,10	0,10	0,15	0,10	0,20
[54] с присадкой	3,0	3,0	3,0	3,0	2,0	2,0	—	—	—	—	—	—
[55] Температура застывания, °С, не выше	−30	−30	−20	−20	−15	−25	−40	−35	−40	−25	−25	−5
[56] Термоокислительная стабильность по методу Папок при 250° С, *мин*, не менее	30	27	30	27	30	30	—	—	—	—	—	—
[57] Коррозия (испытание на пластинках из свинца марки С1 или С2), *г/м²*, не более	—	—	—	—	[56] На бронзе С-30 5	5	10	10	10	10	10	10

1) Index
2) Aviation oil
3) AUSS ...
4) Special oil
5) Diesel oil
6) VTU NP ...
7) Motor oil
8) VTU ...
9) MS-...
10) MS-20S
11) MT-16p
12) Dp-...
13) D-...
14) DSp-...
15) M-12V
16) Without additive
17) With ЦИАТИМ-339 additive
18) Kinematic viscosity, cSt, at 100°C
19) Not below

20) At
21) Ratio of kinematic viscosity at 50°C to kinematic viscosity at 100°C, not larger than
22) Ash, %
23) For oil without additive, no more than
24) For oil with ЦИАТИМ-339 additive, no less than
25) (with 1% VNII NP-360 additive)
26) Coking capacity before addition of additive, %, not above
27) Acid number, mg of KOH to 1 g, not above
28) Without additive
29) With additive
30) Pour point, °C, not above
31) Stability against thermal oxidation by Papok method at 250°C, minutes, not less than
32) Corrosion (test on type S1 or S2 lead plates), g/m^2, not above
33) Automotive oils with additive
34) Special automotive oils
35) Auto-tractor oils
36) ASp-...
37) AKp-...
38) Summer
39) Winter
40) AKZp-...
41) AKzp-...
42) Kinematic viscosity, cSt
43) at 100°C
44) at 0°C, not above
45) Ratio of kinematic viscosity at 50°C to kinematic viscosity at 100°C, not above
46) Ash, %
47) For oil without additive, not above
48) For oil with ЦИАТИМ-339 additive, not less than
49) With 3% NAKS additive, not above
50) Coking capacity before addition of additive, %, not above
51) With 3% NAKS additive
52) Acid number, mg of KOH to 1 g, not above
53) Without additive
54) With additive
55) Pour point, °C, not above
56) Thermal-oxidation stability by Papok method at 250°C, minutes, not below
57) Corrosion (test on type S1 or S2 lead plates), g/m^2, not above
58) On S-30 bronze.

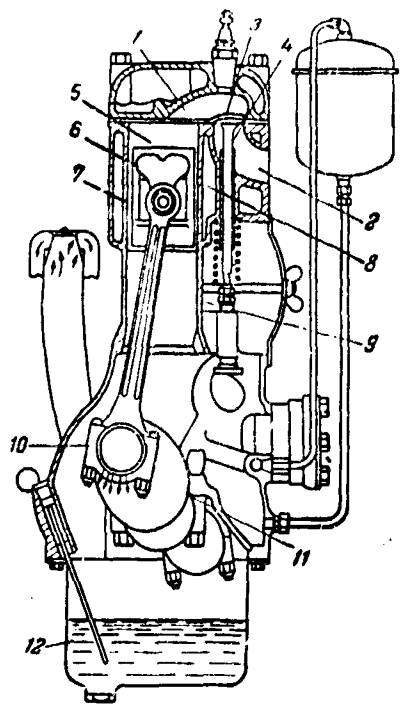


Fig. 6.2. Typical running temperatures in carburetor engine [12]: 1) combustion chamber 2200-2480°C; 2) exhaust gases 540-870°C; 3) exhaust valve head 425-815°C; 4) exhaust valve stem 150-540°C; 5) head of piston 205-425°C; 6) piston-ring zone 150-315°C; 7) piston skirt 95-205°C; 8) cylinder wall (top) 95-370°C; 9) cylinder wall (bottom) 10-150°C; 10) connecting-rod bearings 95-205°C; 11) main bearings 65-175°C; 12) crankcase oil 35-150°C.

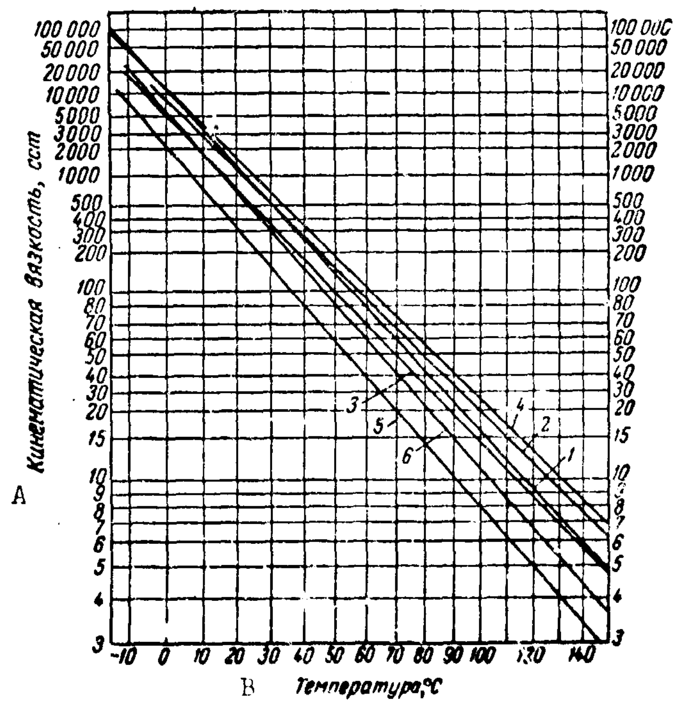


Fig. 6.3. Temperature curves of viscosity for certain aviation and diesel oils: 1) AK-15 (IV-48.7); 2) MS-20 (IV-84.2); 3) MS-14 (IV-83.7); 4) MK-22 (IV-78.1); 5) Dp-8; 6) Dp-11. A) Kinematic viscosity, cSt; B) temperature, °C.

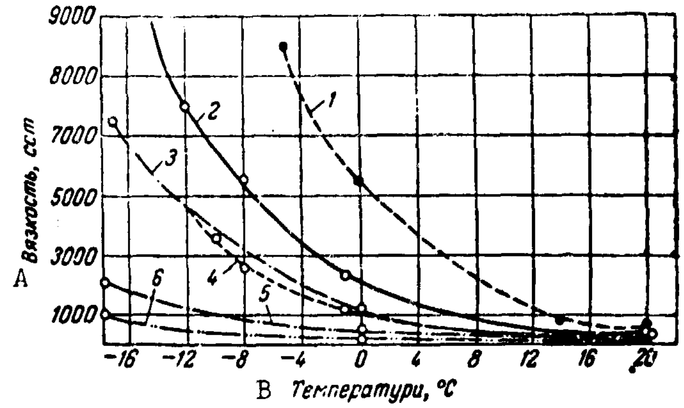


Fig. 6.4. Viscosity-temperature characteristics of domestic and foreign diesel oils at low temperatures: 1) DP-11; 2) DP-8; 3) AKZp-10; 4) SAE-20 (Argentina); 5) SAE-10W (England); 6) SAE-5W (England). A) Viscosity, cSt; B) temperature, °C.

TABLE 6.14

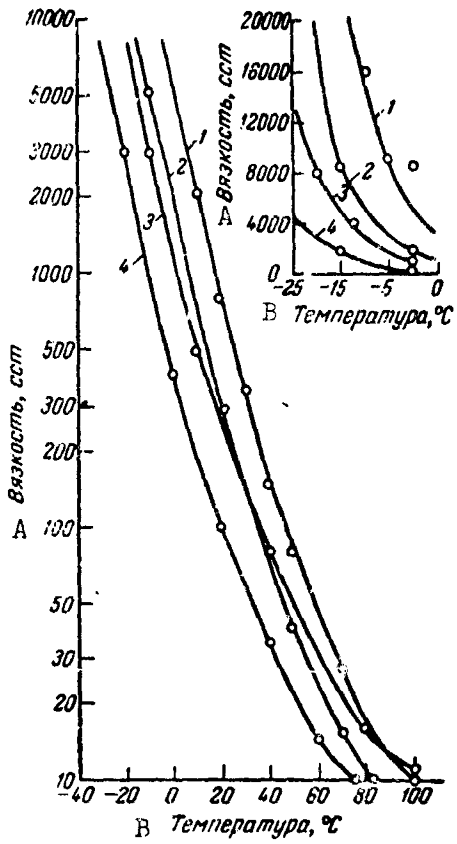
Piston Temperatures in Internal-Combustion Engines [8]

1 Двигатель	2 Температура, °C: 3 верхней части головки поршня	2 Температура, °C: 4 перемычки первого поршневого кольца	1 Двигатель	2 Температура, °C: 3 верхней части головки поршня	2 Температура, °C: 4 перемычки первого поршневого кольца
5 Карбюраторные двигатели			10 Дизели		
6 ЗИЛ-121			11 СМС		
7 при $P_e = 100\%$	198	190	7 при $P_e = 100\%$	338	—
» $P_e = 60\%$	175	169	12 СМД-7		
8 ГАЗ-51			7 при $P_e = 100\%$	228	210*
7 при $P_e = 100\%$	192	187	13 Д-54 (чугунный)		
» $P_e = 60\%$	170	164	7 при $P_e = 100\%$	335	237
9 МЗМА-401			» $P_e = 90\%$	325	232
7 при $P_e = 100\%$	187	180	14 Д-54 (алюминиевый)		
» $P_e = 60\%$	162	147	7 при $P_e = 100\%$	255	210
			7 при $P_e = 90\%$	250	208

*Temperature in first piston-ring groove.

1) Engine
2) Temperature, °C
3) Top of piston head
4) Land of first piston ring
5) Carburetor engines
6) ZIL-121
7) At
8) GAZ-51
9) MZMA-401
10) Diesels
11) SMS
12) SMD-7
13) D-54 (cast iron)
14) D-54 (aluminum).

Fig. 6.5. Viscosity-temperature characteristics of automotive oils: 1) AK-10; 2) AS-5; 3) AKZp-10; 4) AKZp-6. A) Viscosity, cSt; B) temperature, °C.



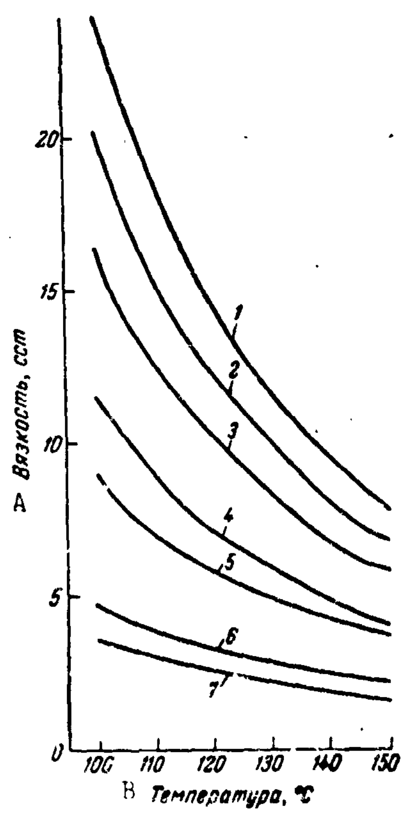


Fig. 6.6. Viscosities of certain oils at high temperatures (according to V.I. Sharapov and Ye.G. Semenido): 1) MK-22; 2) MS-20; 3) MT-16; 4) AK-10; 5) industrial 50; 6) industrial 20; 7) 325-400°C fraction. A) Viscosity, cSt; B) temperature, °C.

most fully by the curve of viscosity as a function of temperature in the temperature range in which the oil is used: from the oil temperature when the engine is started to the temperature developed in the engine parts under various loads (Tables 6.14 and 6.15 and Figs. 6.1 and 6.2). In practice, the determination of high-temperature viscosity is usually limited to a determination at 100°C, since the viscosity change as the temperature rises further is insignificant. Figures 6.3 and 6.4 show the viscosities of certain aviation and diesel oils and Fig. 6.5 those of automotive oils for a broad temperature range; Fig. 6.6 presents viscosity curves of certain oils at temperatures above 100°C.

Flatness of the viscosity-temperature curve is very important. This index determines the starting properties of the oils at low temperatures and their lubricating properties at high operating temperatures. The flatness of oil viscosity-temperature curves are evaluated approximately in American and West European practice by use of the Dean-Davis viscosity index, and in USSR specifications by the ratio of the kinematic viscosities at 50 and 100°C (ν_{50}/ν_{100}). Table 6.13 also gives the values of these indices for certain oils.

Generally, the viscosity index depends on the group chemical composition of the oil; the shallowest viscosity-temperature curves are found for hydrocarbons of the paraffin series and cyclic (naphthenic and aromatic) hydrocarbons with many carbon atoms in the side chains. Values of the viscosity index are given in Table 6.16 for distillates of lubricating oils from various origins and for oils obtained from these distillates by sulfuric acid and selective purification. Selective purification removes polycyclic aromatics and tars from the distillate more thoroughly, and hence the resulting oils have superior viscosity-temperature properties (high viscosity indices). The influence of tars on the viscosity levels of residual and distillate oils is shown in Table 6.17.

TABLE 6.15

Piston Temperatures in Certain Diesels

1 Тип двигателя	2 Температура, °C	
	3 днища поршня (максимальная)	4 поршня в районе верхнего компрессионного кольца
5 Ч-8,5/11	255	150—160
Ч-10,5/13	225	212
Ч-23/30	225—260	220
6 ЧН-18/20	390	240—250
7 2Д-100	520	250

1) Engine type
2) Temperature, °C
3) Top of piston (maximum)
4) Piston, in zone of first compression ring
5) Ch-8.5/11
6) ChN-18/20
7) 2D-100.

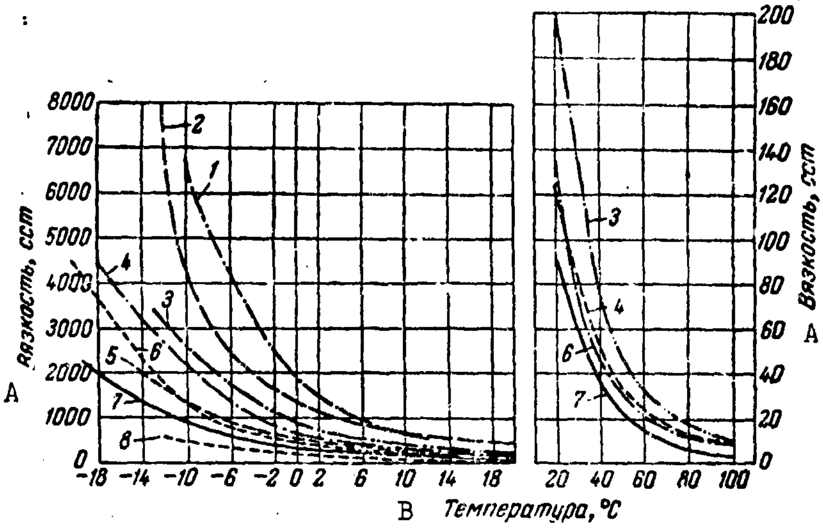


Fig. 6.7. Viscosity-temperature characteristics of multiviscosity oils: 1) D-8; 2) SAE-20; 3) 10W/30; 4) 10W/20; 5) 30W; 6) 5W/30; 7) 5W/20; 8) 5W. A) Viscosity, cSt; B) temperature, °C.

TABLE 6.16

Viscosity Properties and Composition of Distillates and Oils of Type AK-10 Obtained from Certain Typical Petroleums

1 Продукты	2 Вязкость, 3 спз при −20° C	3 спз при −10° C	3 спз при 0° C	4 сст при 20° C	4 сст при 50° C	4 сст при 100° C	ν_{50}/ν_{100}	5 Индекс вязкости	6 Групповой состав (хроматография на силикагеле), %: 7 НПФ	8 АФ	9 ПЦАС	10 Содержание, %: 11 ароматических колец	12 нафтеновых колец	13 парафиновых цепей
14 Дистилляты из нефтей:														
15 балаханской масляной	160 280	26 400	5 270	621	77,2	10,25	7,2	34	67,0	17,2	16,0	8	37	55
16 балаханской тяжелой	321 100	45 100	8 540	834	86,0	10,32	8,1	10	52,6	24,3	20,3	18	40	42
17 бинагадинской	385 300	48 200	9 400	901	91,5	10,87	8,1	21	46,0	27,3	26,6	19	39	42
18 биби-эйбатской	203 800	41 200	7 470	579	70,6	9,55	7,1	30	59,0	23,8	16,0	13	39	48
19 локбатанской	—	51 900	10 370	856	88,4	10,60	8,0	11	58,0	21,0	20,0	17	42	41
20 Масла сернокислотной очистки из нефтей:														
15 балаханской масляной	83 100	15 400	3 540	490	67,5	9,65	6,8	61	67,0	19,8	12,4	4	40	56
16 балаханской тяжелой	175 200	28 580	5 970	608	69,9	9,43	7,0	37	51,0	29,0	18,5	16	35	49
17 бинагадинской	176 600	26 800	5 540	609	70,1	9,47	7,0	35	50,0	34,3	14,0	13	37	50
18 биби-эйбатской	—	34 050	8 440	489	59,9	9,06	6,4	57	60,5	26,8	12,3	6	38	56
19 локбатанской	210 260	23 800	7 620	688	75,6	10,04	7,2	36	62,4	26,0	12,0	11	37	52
21 Масла селективной очистки из нефтей:														
15 балаханской масляной	—	10 420	3 800	460	64,2	9,26	6,5	60	—	—	—	3	33	64
16 балаханской тяжелой	—	23 800	4 945	856	85,9	9,17	6,9	45	—	—	—	9	33	58
17 бинагадинской	—	—	—	—	84,8	9,20	6,9	47	—	—	—	10	36	54
18 биби-эйбатской	—	28 780	5 310	415	57,4	8,69	6,4	61	—	—	—	7	37	56
19 локбатанской	—	18 0[illegible]0	6 090	610	70,7	9,64	7,0	40	—	—	—	7	42	51
22 Товарные масла:														
АК-10	107 820	18 480	4 385	506	61,4	9,98	6,5	41	56,0	26,0	16,7	11	33	56
23 индустриальное 30	33 400	7 410	1 920	281	42,3	7,10	5,3	56	66,6	22,0	11,0	6	36	61

Note. NPF naphthenoparaffinic hydrocarbons; AF aromatic hydrocarbons; PTsAS polycyclic aromatic hydrocarbons and tars.

1) Product
2) Viscosity
3) cp at
4) cSt at
5) Viscosity index
6) Group composition (silica gel chromatography), %

7) NPF
8) AF
9) PTsAS
10) Content, %
11) Aromatic rings
12) Naphthenic rings
13) Paraffinic chains
14) Distillates from petroleum
15) Balakhany oily
16) Balakhany heavy
17) Binagadi
18) Bibi-Eybat
19) Lokbatan
20) Sulfuric acid refined oils from petroleums
21) Selective-refined oils from petroleums
22) Commercial oils
23) Industrial 50.

TABLE 6.17

Influence of Petroleum Tars on Viscosity and Certain Other Properties of Oils [9]

1 Масло	2 Анализ масла					7 Смолы	
	3 плотность ρ_4^{20}	4 вязкость ν_{50}, сСт	5 молекулярный вес	6 коксуемость, %	7 смолы, %	5 молекулярный вес	4 вязкость ν_{50}
8 Балаханский дистиллят	0,913	167	550	0,45	10,1	300	28
9 То же, обессмоленный	0,898	9[illegible]	580	0,10	—	—	—
10 Румынский дистиллят	0,966	275	346	0,15	11,8	480	13
9 То же, обессмоленный	0,958	200	340	0,05	—	—	—
11 Пенсильванский брайтсток	0,898	244	800	1,50	13,3	1700	130
9 То же, обессмоленный	0,884	165	680	0,30	—	—	—
12 Сураханский брайтсток	0,902	248	670	0,85	10,1	400	16
9 То же, обессмоленный	0,894	175	700	0,27	—	—	—
11 Пенсильванский брайтсток	0,902	456	1010	2,90	16,1	—	130
9 То же, обессмоленный	0,879	177	740	0,50	—	—	—
13 Мидконтинентский цилиндрсток	0,930	555	800	0,80	17,4	3000	—
9 То же, обессмоленный	0,903	167	600	0,33	—	—	—

1) Oil
2) Analysis of oil
3) Density
4) Viscosity ν_{50}, cSt
5) Molecular weight
6) Coking capacity
7) Tars
8) Balakhany distillate
9) Same, tars removed
10) Rumanian distillate
11) Pennsylvania bright stock
12) Surakhany bright stock
13) Mid-continent heavy cylinder oil.

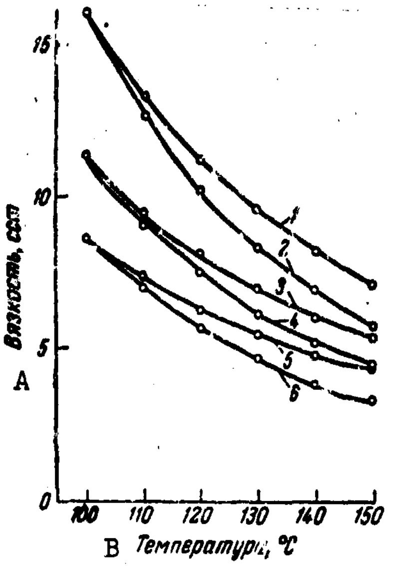


Fig. 6.8. Viscosity properties of normal and thickened oils (after V.I. Sharapov and Ye.G. Semenido): 1) thickened MT-16; 2) commercial MT-16; 3) thickened Dp-11; 4) commercial Dp-11; 5) thickened AS-5; 6) commercial AS-5 (thickened oils are obtained by thickening a narrow petroleum fraction boiling in the 0°C range with polyisobutylene) (see Fig. 6.6). A) Viscosity, cSt; B) temperature, °C.

TABLE 6.18

Viscosity Properties of Normal and Thickened Lubricating Oils [10]

1 Показатели	2 Масло типа АК-6		2 Масло типа АК-10	
	3 загущенное	4 обычное	3 загущенное	4 обычное
5 Вязкость, сст:				
6 при 50° C	28,0	55,5	55,0	71,40
» 100° C	7,99	7,37	13,22	10,53
7 Вязкость с разрушенной структурой, пз:				
6 при −10° C	16	63	25	600
» −20° C	24	282	63	5755
» −30° C	40	1259	159	—
» −40° C	71	—	631	—
» −50° C	170	—	—	—
» −60° C	631	—	—	—
8 Отношение кинематической вязкости при 50° C к кинематической вязкости при 100° C	3,5	7,5	4,2	6,8
9 Индекс вязкости	120	42	120	44
10 Температура, при которой вязкость масла становится равной 100 пз, °C	−43	−12	−25	+5
11 Температура застывания, °C	−62	−34	−48	−11

1) Index
2) Oil type ...
3) Thickened
4) Normal
5) Viscosity, cSt
6) At
7) Viscosity with structure broken down, poises
8) Ratio of 50°C and 100°C kinematic viscosities
9) Viscosity index
10) Temperature at which oil viscosity reaches 100 poises, °C
11) Pour point, °C.

TABLE 6.19

Viscosity of AMT-14p and MT-16p Diesel Oils at Above- and Below-Freezing Temperatures (after Ye.G. Semenido)

1 Масло	2 Вязкость при температуре											
	150° C	130° C	120° C	110° C	100° C	50° C	−5° C	−10° C	−20° C	−25° C	−30° C	−35° C
	3 сст						4 пз					
5 АМТ-14п . . .	5,6	7,8	9,4	11,5	13,9	52,0	10	20	30	50	216	450
6 МТ-16п	5,2	7,7	9,8	12,5	16,0	112,0	120	200	378	1015	—	—

1) Oil
2) Viscosity at temperature of
3) cSt
4) poises
5) AMT-14p
6) MT-16p.

TABLE 6.20

Viscosity of Lubricating Oils as a Function of Dilution by Fuel

1 Автол	2 Вязкость* (в сст) при содержании бензина в автоле, %				
	0	5	10	20	25
3 АКЗп-6	7,0/29,1	5,5/19,3	4,5/14,3	3,2/7,9	2,8/7,0
АК-6	6,4/29,0	4,7/18,2	3,7/12,5	2,5/7,9	2,0/4,8
АКЗп-10	10,5/44,5	8,0/28,6	6,3/20,2	4,2/14,0	3,3/10,2
АК-10	10,4/69,9	8,1/40,5	5,7/23,7	4,0/14,0	3,3/10,1
АК-15	15,8/136,7	11,1/68,0	8,7/35,8	5,2/13,8	4,0/10,0

*Viscosity at 100°C/viscosity at 50°C.

1) Lubricating oil
2) Viscosity* (cSt) at ...% gasoline content in oil
3) AKZp-6.

Motor oils produced by thickening low-viscosity distillate oils with polymers – polyisobutylene, Vinipol, polymethacrylates – have particularly flat viscosity-temperature curves. These oils include AKZp-6 and AKZp-10 lubricating oils, AMT-14p diesel oil and foreign oils of the multigrade type. Tables 6.18 and 6.19 and Figs. 6.5 and 6.7 compare the viscosity characteristics of thickened and normal oils. Thickened oils retain their properties even into the temperature range above 100°C (Fig. 6.8). In use in automotive engines, motor oils are diluted to some extent by the high-boiling fractions of the gasoline.

Table 6.20 shows the change in oil viscosity as a result of

gasoline dilution.

5. STARTING PROPERTIES OF MOTOR OILS

At the starting temperature, the oil must exhibit a certain minimum mobility so that it will reach the lubrication points farthest from the oil pump in the shortest possible time and so as to ensure a resistance moment *M* in rubbing elements such that the starter motor or other starting device will be able to work up the crankshaft speed necessary for starting. Both of these indices are determined by the viscosity of the oil at starting temperature, as well as by the design features of the engine and the power of the storage battery, the voltage across whose terminals falls with decreasing temperature.

TABLE 6.21

Time from Start of Engine to Appearance of Oil at Top of Piston [13]

A № цилиндров	B Масло вязкостью при 26° C, сст	
	1345	252
1	10 мин (C) 27 сек (D)	3 мин 0 сек
2	29 » 5 »	9 » 0 »
3	30 » 0 »	12 » 14 »
4	10 » 10 »	5 » 43 »
5	3 » 25 »	2 » 55 »
6	17 » 20 »	9 » 0 »

A) Number of cylinders
B) Viscosity of oil at 26°C, cSt
C) Minutes
D) Seconds.

TABLE 6.22

Viscosity of Certain Oils at Low Temperatures (after M.P. Volarovich [13])

1 Масло	2 Вязкость при -20° C, ст	3 Температура, при которой вязкость равна 85 ст
4 Машинное 2 . . .	270	−12,3
5 Цилиндровое 50	1120	−1,1
АК-10 . . .	1420	−3,0
6 АС-10	560	−6,0
7 АКЗп-6 . . .	41,1	−27,0
АКЗп-10 . .	68,0	−22,0

1) Oil
2) Viscosity at 20°C, St
3) Temperature at which viscosity reaches 85 St
4) Machine 2
5) Cylinder 50
5) AS-10
7) AKZp-6.

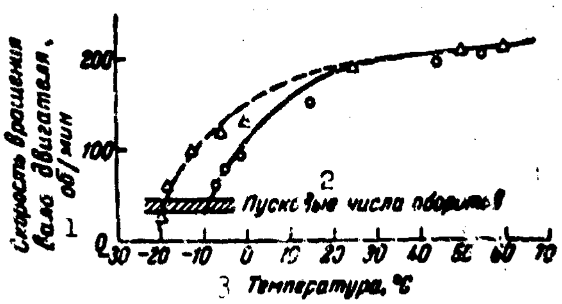


Fig. 6.9. Influence of oil temperature on speed of GAZ 51 engine (ST-08 starter running off two 3-ST-70 batteries) (after M.A. Senichkin and P.G. Filatov): ---- AKZp-10; —— AKp-5. 1) Engine shaft speed, revolutions per minute; 2) starting rev/min; 3) temperature, °C.

TABLE 6.23

Starting Properties of Oils in GAZ-51 Engine

1 Показатели	2 Масла			
	3 АС-5	АК-6	4 АКЗп-10	АКЗп-6
5 Вязкость (в спз) при температуре:				
—10° C	6 849	5 510	2 450	1 250
—20° C	31 431	22 260	8 140	4 080
—30° C	—	113 620	39 400	21 290
6 Предельная температура прокачиваемости, °C	—19	—18	—28	—32
7 Минимальная температура запуска (35—40 об/мин коленчатого вала), °C	—13	—17	—24	—28

1) Index
2) Oil
3) AS-5
4) AKZp-10
5) Viscosity (centipoise) at temperature of
6) Limiting pumpability temperature, °C
7) Minimum starting temperature (35-40 crankshaft rev/min), °C.

The influence of viscosity on the time required for oil to appear at the top of the piston after the engine has started is shown in Table 6.21. The viscosities of a wide variety of aviation oils range from 350-450 St at the pumpability temperature, while the viscosity at which the engine can be started may not exceed 90-100 St. MK-22 oil has this viscosity at about 2°C, and MS-14 oil at -10°C. According to some sources [11], the maximum starting viscosity of automotive oil is 80-90 St, and according to others [12] it may range up to 200 St. The difference is apparently due to differences in the design and starting speeds of the engines. Table 6.22 shows the temperatures at which the viscosities of various oils reach the 85-St maximum value for engine starting.

The starting speed is 35-50 rev/min for carburetor engines, 50-90 rev/min for engines with compression ignition and direct injection, 120-150 rev/min for swirl-chamber engines, and 150-200 rev/min for divided-chamber engines. Figures 6.9-6.10 show the influence of oil temperature and viscosity on engine speed. Tables 6.23-6.25 and Fig. 6.11 show the limiting values of oil pumpability temperature. In solving starting-viscosity problems, it is necessary to consider the drop in the voltage across battery terminals with declining temperature.

Excessively high oil viscosity and the related decrease in pumpability at starting causes accelerated engine wear (Figs. 6.12-6.13). For a warmed-up engine, wear usually decreases with increasing oil viscosity.

Selection of the optimum viscosity is determined by engine operating conditions: with frequent starts and stops, as under the conditions of urban automobile traffic, preference should be given

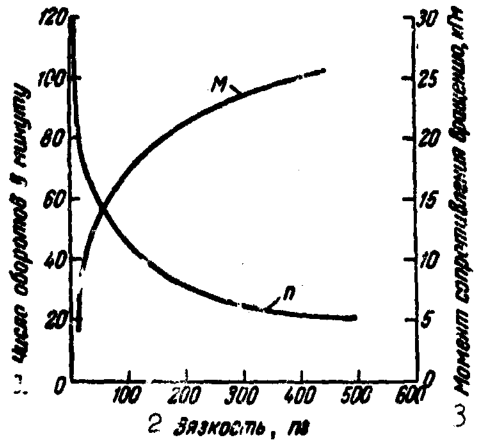


Fig. 6.10. Drag torque (M) and crankshaft speed (n) as functions of oil dynamic viscosity (after S.F. Rubinshteyn). 1) Revolutions per minute; 2) viscosity, poises; 3) drag torque, kg-m.

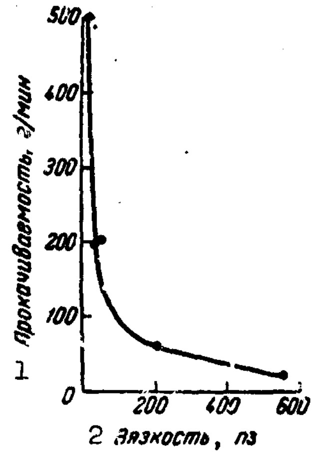


Fig. 6.11. Pumpability of oil in lubricating system of GAZ-51 engine as a function of oil dynamic viscosity (after S.F. Rubinshteyn). 1) Pumpability, g/min; 2) viscosity, poises.

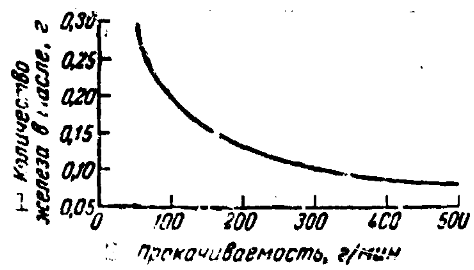


Fig. 6.12. Wear in GAZ-51 engine over three starts and warmups (in g of iron) as a function of oil pumpability in lubricating system (after S.F. Rubinshteyn). 1) Amount of iron in oil, g; 2) pumpability, g/min.

TABLE 6.24

Minimum Engine Starting Temperatures (°C) [14]

1 Масло	2 ГАЗ-51	3 ЗИЛ-120 со стартером: 4 СТ-15	СТ-45
5 Автол дистиллятный вязкостью при 50° С:			
6 2,5° ВУ	−30	−18	—
4,0 °ВУ	−23	−11	—
7 Автол загущенный вязкостью при 50° С:			
4,0° ВУ	−27	−14	−23

1) Oil
2) GAZ-51
3) ZIL-120 with starter
4) ST-15
5) Distillate lubricating oil with 50°C viscosity of
6) 2.5°VC
7) Thickened lubricating oil with 50°C viscosity of.

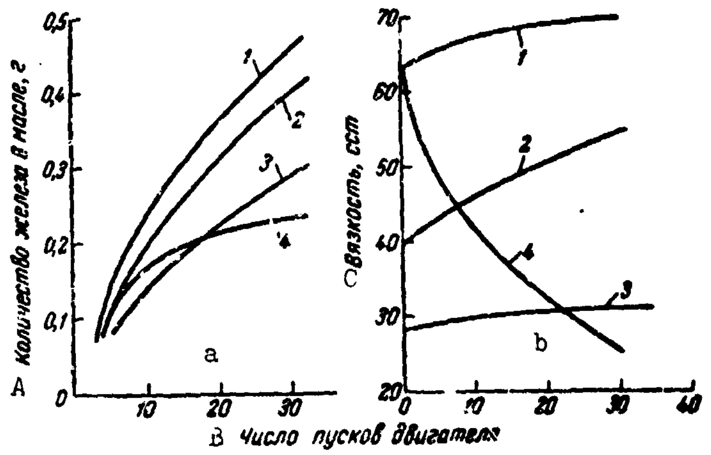


Fig. 6.13. Wear of GAZ-42 engine in starting and warming up on oils of various viscosities: a) wear as a function of number of engine starts; b) change in oil viscosity (at 50°C) in progress of test; 1, 2, 3) starting and warmup on generator gas; 4) starting and warmup on gasoline. A) Amount of iron in oil, g; B) number of engine starts; C) viscosity, cSt.

TABLE 6.25

Limiting Viscosities that Ensure Pumpability of Oils and Starting of Engines [15]

1 Двигатель	2 Вязкость масел (в сст), обеспечивающая	
	3 прокачиваемость	4 запуск
5 ГАЗ-51	25 000—30 000	18 000—20 000
6 ЗИЛ-120:		
7 стартер СТ-15	11 000	3 000—4 000
стартер СТ-45	30 000	11 000

1) Engine
2) Oil viscosities (in cst) that ensures
3) Pumpability
4) Starting
5) GAZ-51
6) ZIL-120
7) ST-15 starter.

to low-viscosity oils, since starting wear predominates in this case. Under the conditions of extended continuous operation, wear is reduced by the use of higher-viscosity oils, which maintain a certain minimum viscosity level at the highest operating temperatures.

6. CORROSION PROPERTIES OF MOTOR OILS

The problem of corrosion of the antifriction alloys used in the bearings of internal-combustion engines arose in connection with the extensive replacement of tin babbitt by other alloys differing from it in having higher fatigue strength and better mechanical properties, but considerably inferior to it in anticorrosion stability. This pertains especially to such alloys as copper-lead, lead babbitt and cadmium-base alloys. Tables 6.26 and 6.27 give the compositions of typical alloys used at the present time in the bearings of internal-combustion engines.

The lead component of the alloys is least stable to attack by the corrosively aggressive products present in the oils (Table 6.28). Hence the corrosion properties of oils are evaluated with respect to lead in the methods of the NAMI (DK-2-NAMI) and Yu.A. Pinkevich that have been adopted in our country.

Table 6.13 presents norms for the corrosiveness of motor oils with respect to lead.

The corrosion properties of the oil depend on the presence of corrosively aggressive components (naphthenic acids) in them and on the tendency of the oils to form corrosive agents as a result of oxidation (carboxylic and hydroxycarboxylic acids), as determined by the group chemical composition of the oil. Tables 6.29 and 6.30 present the corrosion properties of distillates and certain experimental and commercial motor oils. Oils from sulfur-containing petroleums usually show less corrosive aggressiveness (Table 6.31).

TABLE 6.26

Compositions of Typical Bearing Alloys [12]

1 Сплав	2 Примерный состав	3 Структура
4 Оловянистый баббит . .	3% Cu, 7—8% Sb, 5 остальное Sn	6 Однородный сплав
7 Свинцовистый баббит	1—10% Sn, 15% Sb, 5 остальное Pb	8 То же
9 Кадмиево-серебряный .	0,75—2,0% Cu, 0,25—0,5% Ag, остальное Cd	»
10 Кадмиево-никелевый . .	1,0—1,5% Ni; 5 остальное Cd	»
11 Медно-свинцовый . . .	25—40% Pb, немного Ag, 12 остальное Cu	13 Медная матрица (губка), заполненная свинцом
14 То же, с покрытием . .	8 То же	15 То же, но на поверхность нанесен слой свинца или баббита
16 То же, модифицированный	»	17 Медно-никелевая матрица, заполненная свинцовистым баббитом с таким же покрытием
18 Алюминиевый	19 6,5% Sn, 1% Cu, 0,5—1% Ni, 2,5% Si (иногда), остальное Al	20 Однородный сплав
21 Серебряный с покрытием	Довольно чистое серебро с покрытием из свинца или свинца и индия 22	Чистый металл с покрытием 23

1) Alloy
2) Approximate composition
3) Structure
4) Tin babbitt
5) Remainder
6) Homogeneous alloy
7) Lead babbitt
8) Same
9) Cadmium-silver
10) Cadmium-nickel
11) Copper-lead
12) 25-40% Pb, small amount of Ag, remainder Cu
13) Copper matrix (sponge) filled with lead
14) Same, coated
15) Same, but with a layer of lead or babbitt applied to the surface
16) Same, modified
17) Copper-nickel matrix filled with lead babbitt, with the same coating
18) Aluminum
19) 6.5% Sn, 1% Cu, 0.5-1% Ni, 2.5% Si (sometimes), remainder Al
20) Homogeneous alloy
21) Silver with coating
22) Silver of rather high purity with lead or lead-and-indium coating
23) Pure metal with coating.

TABLE 6.27

Properties of Poured Inserts of Various Types (Optimum Rating 100) [12]

1 Показатели	2 Сплавы						
	3 оловянистый баббит	4 свинцовистый баббит	5 кадмиевые	6 медно-свинцовые	7 медно-свинцовые с покрытием	8 алюминиевые	9 серебряные с покрытием
10 Сопротивляемость усталости	8	12	30	47	47	80	100
11 Приработка	83	83	57	14	100	53	100
12 Вдавливаемость	100	73	60	38	51	18	12
13 Противозадирные свойства	100	93	57	38	72	86	72
14 Устойчивость против коррозии	100	75	39	25	83	100	100
15 Твердость	100	100	85	38	100	38	12
16 Термостойкость	7	10	11	16	16	39	100
17 Теплопроводность	17	8	23	70	67	52	48

1) Index
2) Alloy
3) Tin babbitt
4) Lead babbitt
5) Cadmium
6) Copper-lead
7) Coated copper-lead
8) Aluminum
9) Coated silver
10) Fatigue strength
11) Running-in
12) Embeddability
13) Antiscoring properties
14) Corrosion stability
15) Hardness
16) Thermal stability
17) Thermal conductivity.

TABLE 6.28

Change in Properties of Copper-Lead Alloy Poured Bearing Inserts as a Result of Corrosion [16]

1 Вкладыш	2 Состав заливки, %					
	Cu	Pb	Sn	Fe	P	Ni
3 Новый	65,85	33,85	0,60	0,16	4 Следы	
5 Разрушенный	95,40	0,64	0,49	1,26	0,02	0,15

1) Insert
2) Composition of casting, %
3) New
4) Traces
5) Corroded.

TABLE 6.29

Corrosion Properties of Certain Motor Oils Without Additives [17]

1 Масло	2 Коррозия по Пинкевичу, г/м²		5 Кислотное число мг KOH на 1 г	
	3 на свинце	4 на свинцовистой бронзе	6 до окисления	7 после окисления
8 Авиационное:				
МК-22	2,0	0,7	0,05	0,17
9 МС-14	45,2	15,0	0,08	0,14
10 Дизельное:				
11 Д-11 (смесь МК-22 и индустриального 50)	67,3	30,0	0,06	0,19
12 Д-11 из эмбенских нефтей	108,0	37,0	0,42	0,50
13 Индустриальное 50	82,8	27,1	0,14	0,55
АК-10	83,8	20,0	0,19	0,50

1) Oil
2) Pinkevich corrosion, g/m^2
3) On lead
4) On lead bronze
5) Acid number, mg of KOH to 1 g
6) Before oxidation
7) After oxidation
8) Aviation
9) MS-14
10) Diesel
11) D-11 (mixture of MK-22 and industrial 50)
12) D-11 from Emba petroleums
13) Industrial 50.

TABLE 6.30

Corrosive Properties of Distillates and Oils from Sulfuric Acid and Selective Refining [18] of Baku and Emba Petroleums

1 Продукты	2 Коррозия свинцовых пластинок, г/м²		5 Коррозия пластинок свинцовистой бронзы, г/м²		
	3 аппарат НАМИ 20 ч	4 аппарат Пинкевича 50 ч	3 аппарат НАМИ 20 ч	4 аппарат Пинкевича 50 ч	6 Вымывание свинца из слоя 0,2 мм, %
7 Дистилляты					
8 Балаханская					
9 масляная нефть . . .	305	303	—	113	83
10 тяжелая нефть . . .	314	280	80	92	79
11 Бинагадинская	317	183	43	77	83
12 Биби-эйбатская	163	111	9	39	53
13 Локбатанская	297	237	70	54	—
14 Масла сернокислотной очистки					
8 Балаханская					
9 масляная	54	59	2	6	8
10 тяжелая	83	60	1	9	10
11 Бинагадинская	6	7	1	4	12
12 Биби-эйбатская	86	66	1	10	1
13 Локбатанская	89	70	1	10	7
15 Масла селективной очистки (фурфуролом)					
8 Балаханская					
9 масляная	50	50	11	36	—
10 тяжелая	84	70	4	17	—
11 Бинагадинская	—	6	—	7	—
12 Биби-эйбатская	7	12	1	3	—
13 Локбатанская	20	13	1	8	—
16 Масла селективной очистки (фенолом)					
8 Балаханская					
9 масляная	—	—	—	70	60
10 тяжелая	—	—	—	51	50
11 Бинагадинская	—	—	—	44	41
13 Локбатанская	—	—	—	49	58
17 Товарные и опытные масла					
18 Автол из эмбенских нефтей	67	68	8	18	—
19 Индустриальное 50 . . .	74	53	6	30	44
20 АК-10 товарный	110	71	10	39	45
21 Авиационное МК-22 товарное	2	—	1	3	11
22 Смесь МК + индустриальное 50	—	46	—	6	—

1) Product
2) Corrosion of lead plates, g/m²
3) NAMI apparatus, 20 h
4) Pinkevich apparatus, 50 h
5) Corrosion of lead-bronze plates, g/m²
6) % of lead washed out of 0.2-mm layer
7) Distillates

8) Balakhany
9) Oily petroleum
10) Heavy petroleum
11) Binagadi
12) Bibi-Eybat
13) Lokbatan
14) Sulfuric-acid-refined oils
15) Selectively refined (furfural) oils
16) Selectively refined (phenol) oils
17) Commercial and experimental oils
18) Lubricating oil from Emba petroleums
19) Industrial 50
20) AK-10 commercial
21) MK-22 commercial aviation
22) Mixture of MK + industrial 50.

TABLE 6.31

Corrosion Properties of Oils and Oily Fractions from Sulfur-Bearing Petroleums [19, 20] (by method of Yu.A. Pinkevich)

[1] Масла или фракции	[2] Содержание серы, %	[3] На свинцовистой бронзе		[6] На освинцованной электролитической свинцовистой бронзе	
		[4] коррозия, $г/м^2$	[5] кислотное число, мг KOH на 1 г	[4] коррозия, $г/м^2$	[5] кислотное число, мг KOH на 1 г
[7] Автол 6 селективной очистки туймазинской девонской нефти	1,69	1,97	1,25	42,21	2,5
[8] Фракция нафтеновых углеводородов автола 6	[9] Нет	74,61	1,96	144,4	3,84
[10] Фракция ароматических углеводородов ($n_D^{20} = 1,5100$) автола 6	1,60	2,93	1,0	116,8	3,8
[11] Фракция ароматических углеводородов ($n_D^{20} = 1,5405$) автола 6	2,94	0	0,42	20,4	2.7
[12] Дизельное ДС-11 из смеси девонских сернистых нефтей	1,00	1,6	0,17	17,0	—
[13] Дизельное МТ-16 из смеси девонских сернистых нефтей	1,11	—	—	9,0	—

1) Oil or fraction
2) Sulfur content, %
3) On lead bronze
4) Corrosion, g/m^2
5) Acid number, mg of KOH to 1 g
6) On leaded electrolytic lead bronze
7) Lubricating oil 6 from selective refinement of Tuymazy Devonian petroleum
8) Naphthenic hydrocarbon fraction of lubricating oil 6
9) None
10) Aromatic hydrocarbon fraction (n_D^{20} = 1.5100) of lubricating oil 6
11) Aromatic hydrocarbon fraction (n_D^{20} = 1.5405) of lubricating oil 6
12) Diesel DS-11 from mixture of Devonian sulfur-containing petroleums
13) Diesel MT-16 from mixture of Devonian sulfur-bearing petroleums.

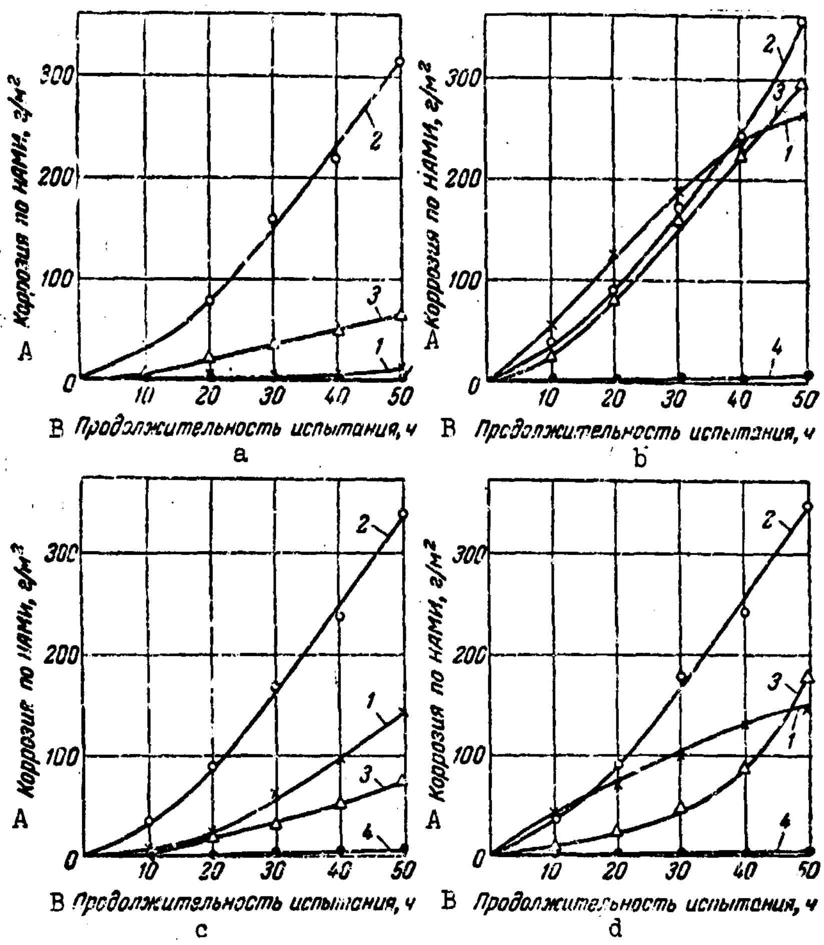


Fig. 6.14. Corrosive aggressiveness of oil hydrocarbon fractions as a function of test time (according to V.K. Novikov): a) MT-16 from sulfurous petroleums; b) MT-16 from Emba petroleums; c) DS-11 from sulfurous petroleums; d) industrial 50; 1) original oils; 2) naphthenoparaffinic hydrocarbons; 3) aromatic hydrocarbons desorbed by isooctane; 4) aromatic hydrocarbons desorbed by benzene. A) NAMI corrosion, g/m²; B) test time, h.

The naphthenoparaffinic fractions of the oils, which are least stable to oxidation, exhibit the highest corrosive aggressiveness (Fig. 6.14). Aromatics are considerably less aggressive.

7. STABILITY OF OILS AGAINST OXIDATION

The stability of oils against oxidation by atmospheric oxygen at elevated temperatures is an important operational characteristic. This index determines the tendency of the oil to form corrosively aggressive acidic products that dissolve in it and insoluble oxidation products that are deposited on engine parts in the form of varnishes, sludge and scale. Formation of insoluble products results in fouling of the engine and causes burning of piston rings, which, in turn, accelerates wear and is detrimental to other technical characteristics of the engine.

TABLE 6.32

Operational Properties of Certain Motor Oils [21]

1 Масло	2 Моторные свойства при 250° С *			6 Критическая температура лакообразования, °С **	7 Термическая стабильность при 250° С, мин ***	8 Лаковый остаток при 260° С, %	9 Коэффициент лакообразования	10 Моющие свойства по ПЗВ, баллы ****
	3 испаряемость, %	4 рабочая фракция, %	5 лак, %					
11 АС-9,5 Новокуйбышевского завода . .	79	9	12	240	29	46	1,6	4,0
12 ДС-11 Новокуйбышевского завода . .	69	28	3	250	29	32	1,1	4,0—4,5
13 МС-20 Грозненского завода	59	32	9	240	23 (260° С)	40	2,0	4,0—4,5
14 МС-20 Новокуйбышевского завода . .	44	54	2	255	31 (260° С)	43	1,4	—
15 МК-22 Бакинское . .	52	45	3	245	21 (260° С)	40	2,0	3,5

*AUSS 5737-53 method.
**AUSS 9787-61 method.
***AUSS 9352-60 method.
****AUSS 5726-53 method.

1) Oil
2) Motor properties at 250°C*
3) Vaporizability, %
4) Working fraction, %
5) Varnish, %
6) Critical varnish-formation temperature, °C**
7) Thermal stability at 250°C, min***
8) Varnish residue at 260°C, %
9) Varnish-forming coefficient
10) Detergent properties according to PZV, points****
11) AS-9.5 from Novo-Kuybyshev refinery
12) DS-11 from Novo-Kuybyshev refinery
13) MS-20 from Groznyy refinery
14) MS-20 from Novo-Kuybyshev refinery
15) MK-22 Baku.

TABLE 6.33

Varnish Formation by Commercial Oils and Hydrocarbon Groups Separated from Them [22] (method of S.K. Kyuregyan at 250°C)

A Продукты	Период лакообразования, B мин	A Продукты	Период лакообразования, B мин
C МК-20 из сураханской отборной нефти	12	D Нафтено-парафиновая фракция	6
F Полициклическая ароматическая фракция	26	E Малоциклическая ароматическая фракция	9
G МС-20 из карачухуро-сураханской нефти	10	I МТ-16 из сернистых нефтей	12,5
D Нафтено-парафиновая фракция	5	D Нафтено-парафиновая фракция	6,5
E Малоциклическая ароматическая фракция	8	E Малоциклическая ароматическая фракция	11
F Полициклическая ароматическая фракция	17	F Полициклическая ароматическая фракция	17
H МТ-16 из эмбенской нефти	8	J ДС-11 из сернистых нефтей	10
D Нафтено-парафиновая фракция	5	D Нафтено-парафиновая фракция	5
E Малоциклическая ароматическая фракция	6	E Малоциклическая ароматическая фракция	9
F Полициклическая ароматическая фракция	13,5	F Полициклическая ароматическая фракция	10

A) Product
B) Varnish-formation period, min
C) MK-20 from Surakhany select petroleum
D) Naphthenoparaffinic fraction
E) Oligocyclic aromatic fraction
F) Polycyclic aromatic fraction
G) MS-20 from Karachukhur-Surakhany petroleum
H) MT-16 from Emba petroleum
I) MT-16 from sulfur-containing petroleums
J) DS-11 from sulfur-containing petroleums.

TABLE 6.34

Results of Evaluation of Oil Use Properties by GSM-20 Method [23]

1 Масло	Лакообразование за 5 ч, % черного лака 2	Работоспособность, ч 3	Коррозия за 10 ч, г/м² 4	Моющие свойства по ПЗВ, баллы 5
6 МК-22 бакинское	80	10	45	3,5
7 МС-20 из сернистых нефтей	50	20	30	3,0
8 МС-20 из жирновско-коробковской нефти	75	10	25	3,5
9 МС-20 из карачухуро-сураханской нефти:				
10 образец 1	90	5	65	3,0
образец 2	100	5	50	4,0—4,5
11 МТ-16 из сернистых нефтей	55	12	20	3,0—3,5
12 МТ-16 из жирновско-коробковской нефти	75	10	25	3,0—3,5
13 МТ-16 из карачухуро-сураханской нефти	100	5	65	3,0—3,5
14 МТ-16 из эмбенской нефти	100	5	60	4,0—4,5
15 ДС-11 из сернистых нефтей	65	8	70	—
16 Индустриальное 50 из балаханской масляной нефти	35	9	85	—
17 АС-9,5 из сернистых нефтей	75	9	50	4,0
18 АС-5 из сернистых нефтей	100*	4	60	—

*After 4 hours.

1) Oil
2) Varnish formation in 5 hr, % black varnish
3) Useful life, h
4) Corrosion in 10 h, g/m²
5) Detergent properties according to PZV, points
6) MK-22 Baku
7) MS-20 from sulfur-containing petroleums
8) MS-20 from Zhirnovsk-korobkovsk petroleum
9) MS-20 from Karachukhur-Surakhany petroleum
10) Specimen ...
11) MT-16 from sulfur-containing petroleums
12) MT-16 from Zhirnovsk-korobkovsk petroleum
13) MT-16 from Karachukhur-Surakhany petroleum
14) MT-16 from Emba petroleum
15) DS-11 from sulfur-containing petroleums
16) Industrial 50 from Balakhany oily petroleum
17) AS-9.5 from sulfur-containing petroleums
18) AS-5 from sulfur-containing petroleums.

TABLE 6.35

Physicochemical and Operational Properties of MT-16 Base Oils Obtained from Various Raw Materials [24]

1 Показатели	2 Базовые масла МТ-16						
	3 из эмбенских нефтей Ярославского завода	4 из сернистых нефтей Ново-куйбышевского завода	5 из эмбенских нефтей Орского завода	6 из карачухуро-сураханской нефти	7 из жирновско-коробковской нефти	8 из сернистых нефтей Ново-Уфимского завода	
						9 остаточное	10 смешанное
11 Вязкость кинематическая при 100° С, *сст*	16,7	17,3	17,2	16,2	15,9	16,9	16,3
12 Отношение кинематической вязкости при 50° С к кинематической вязкости при 100° С	6,5	6,9	6,6	7,2	7,7	6,9	6,5
13 Температура застывания, ° С	−17	−18	−23	−27	−28	−12	−15
14 Температура вспышки (в открытом тигле), °С	230	253	240	222	228	249	241
15 Кислотное число, *мг* КОН на 1 *г*	0,15	0,00	0,08	0,08	0,06	0,00	0,01
16 Коксуемость, %	0.50	0,35	0,40	0,40	0,40	0,53	0,57
17 Зольность, %	0,009	0,005	0,004	0,004	0,001	18 Отс.	0,008
19 Коррозия по Пинкевичу, *г/м²*	55	8	8	38	16	17	16
20 Моторные свойства при 250° С, %:							
21 испаряемость	67	49	62	69	64	48	53
22 рабочая фракция	17	47	31	19	32	51	46
23 лак	16	4	7	12	4	1	1
24 Антиокислительные свойства							
25 термоокислительная стабильность при 260° С, %	18	34	22	24	25	32	25
26 лаковый остаток при 260° С, %	34	40	32	30	30	36	34
27 коэффициент лакообразования при 260° С	1,9	1,2	1,4	1,2	1,2	1,1	1,4
28 критическая температура лакообразования, ° С	235	255	245	245	245	255	255
29 моющие свойства по ПЗВ, баллы	4—4,5	3—3,5	3,5	3—3,5	3—3,5	2,5—3	4,0
30 Испытания по методу ГСМ-20:							
31 лакообразование за 5 *ч*, % черного лака	100	55	100	95	75	60	50
32 коррозия за 10 *ч*, *г/м²*	61	18	—	67	25	31	45

1) Index
2) MT-16 base oils
3) From Emba petroleums, Yaroslavl refinery
4) From sulfur-containing petroleums, Novo-Kuybyshev refinery
5) From Emba petroleums, Orsk refinery
6) From Karachukhur-Surakhany petroleum
7) From Zhirnovsk-korobkovsk petroleum
8) From sulfur-containing petroleums, Novo-Ufa refinery
9) Residual
10) Mixed
11) Kinematic viscosity at 100°C, cSt
12) Ratio of 50°C to 100°C kinematic viscosities
13) Pour point, °C
14) Flash point (open crucible), °C
15) Acid number, mg of KOH to 1 g
16) Coking capacity, %
17) Ash, %
18) None
19) Pinkevich corrosion, g/m²
20) Motor properties at 250°C, %
21) Vaporizability
22) Working fraction
23) Varnish
24) Antioxidation properties
25) Thermal-oxidation stability at 260°C, %
26) Varnish residue at 260°C, %
27) Coefficient of varnish formation at 260°C
28) Critical varnish-forming temperature, °C
29) PZV detergent properties, points
30) Tests by GSM-20 method
31) Formation of varnish in 5 h, % black varnish
32) Corrosion in 10 h, g/m².

In the technical specifications for commercial motor oils (see Table 6.13), stability against oxidation is indirectly characterized only by the thermal-oxidation stability index according to K.K. Papok's method (AUSS 9352-60) and directly by the corrosion coefficient according to Yu.A. Pinkevich (AUSS 5162-49). Experience has shown that these two indices are insufficient for exhaustive characterization of this property of the oils. In view of this, a number of rating methods have been proposed, and, in the aggregate, they permit a more complete evaluation of oil antioxidation stability. A comparative evaluation made by these methods for a number of motor oils of various origins appears in Tables 6.32 and 6.33.

The antioxidation stability of an oil can also be evaluated by testing the oil in a special engine. The results of such rating of a series of oil in the IT9-3 engine by the GSM-20 method are given in Table 6.34.

Table 6.35 presents the results of comparative studies and tests of a number of specimens of MT-16 diesel oil produced from various raw materials.

8. GROUP CHEMICAL COMPOSITION AND CERTAIN PHYSICOCHEMICAL PROPERTIES OF COMMERCIAL MOTOR OILS

Depending on origin, production method and refining method, the operational properties of oils of the same grade may vary to a certain degree. Data characterizing the properties of typical motor oils obtained from various raw materials or by different processes are given in Tables 6.36-6.39.

TABLE 6.36

Physicochemical Properties and Group Chemical Composition of Lubricating Oils [25]

A Показатели	B Масла сернокислотной очистки из бакинских нефтей		D Масло АС-9,5 селективной очистки из сернистых нефтей				
	АК-10	C индустриальное 50	E дистиллятное	F компаундированное	G углубленной очистки	H сернокислотной доочистки	I адсорбционной доочистки
J Плотность ρ_4^{20} . . .	0,9117	0,9023	0,8916	0,8854	0,8825	0,8300	0,8815
K Коэффициент преломления n_D^{20} . .	1,5090	1,4982	1,4955	1,4940	1,4894	1,4893	1,4885
L Анилиновая точка, °C	88	98	97	99	102	103	105
M Вязкость кинематическая при 100° C, *сст*	10,7	8,46	11,0	11,35	9,54	9,66	9,77
N Индекс вязкости .	42	60	83	92	90	95	96
O Сера, %	0,25	0,20	1,20	1,15	0,97	0,93	0,83
P Кислотное число, *мг* KOH на 1 *г* . . .	0,13	0,10	0,06	0,06	0,08	0,02	0,02
Q Коррозия по Пинкевичу, *г/м²*	58	70	18	28	9	4	2
R Групповой химический состав, %:							
S нафтеново-парафиновые . . .	56,5	66	—	57	60	62	61,3
T ароматические .	25	22,5	—	26	27	29,5	31,0
U тяжелые ароматические . .	15	10	—	13	10	6,4	6,0
V смолы	1,3	1	—	1,6	1	0,8	1,0

A) Index
B) Oil sulfuric-acid-refined from Baku petroleums
C) Industrial 50
D) AS-9.5 oil selectively refined from sulfur-containing petroleums
E) Distillate
F) Compounded
G) Deep-refined
H) Sulfuric acid postrefinement
I) Adsorption postrefinement
J) Density
K) Refractive index
L) Aniline point
M) Kinematic viscosity at 100°C, cSt
N) Viscosity index
O) Sulfur, %
P) Acid number, mg of KOH to 1 g
Q) Pinkevich corrosion, g/m²
R) Group chemical composition, %
S) Naphthenoparaffinic
T) Aromatic
U) Heavy aromatic
V) Tars.

TABLE 6.37

Characteristics of Hydrocarbon Groups Separated from DS-8 and DS-14 Oils [26, 27]

1 Группы углеводородов	2 Удельная дисперсия	3 Плотность ρ_4^{20}	4 Показатель преломления n_D^{20}	5 Вязкость кинематическая, сст: 6 при 50° С	6 при 100° С	7 Индекс вязкости	8 Сера, %
9 Масло ДС-8							
10 Нафтено-парафиновые	97	0,8643	1,4755	27,95	6,58	109	0,01
11 Ароматические							
12 легкие	112	0,8900	1,4915	40,02	7,99	89	0,41
13 средние	139	0,9329	1,5170	69,60	10,15	42	1,45
14 тяжелые	162	0,9778	1,5390	244,13	19,39	—26	3,6
15 Масло ДС-14 *							
10 Нафтено-парафиновые	90—101	0,8610—0,8798	1,4722—1,4830	—	9,64—11,99	97—115	—
11 Ароматические							
12 легкие	102—120	0,8807—0,9107	1,4848—1,5036	—	12,09—17,6	87—96	—
13 средние	121—155	0,9052—0,9504	1,5034—1,5322	—	15,95—39,23	—	—
14 тяжелые	160	0,9600—0,9852	1,5340—1,5560	—	36,52—60,37	—2 ÷ —9 15	—

*The values given are the extremes for DS-14 oils obtained by mixing various distillate and residual components [27].

1) Hydrocarbon group
2) Specific dispersion
3) Density
4) Refractive index
5) Kinematic viscosity, cSt
6) At
7) Viscosity index
8) Sulfur, %
9) DS-8 oil
10) Naphthenoparaffinic
11) Aromatic
12) Light
13) Medium
14) Heavy
15) DS-14 oil*
16) To.

TABLE 6.38

Physicochemical Properties and Group Chemical Composition of Diesel Oils from Eastern Sulfur-Containing Petroleums* [26, 27]

1 Показатели	2 Масла	
	3 ДС-8	ДС-14 **
4 Плотность ρ_4^{20}	0,8910	—
5 Вязкость кинематическая, *сст*		
6 при 50° C	42,0	—
при 100° C	8.13	13,17—14,63
7 Индекс вязкости	85	85—90
8 Показатель преломления n_D^{20}	1,4820	—
9 Сера, %	0,31	0,85—1,1
10 Групповой химический состав, %:		
11 нефтено-парафиновые	52,40	48,84—54,90
12 легкие ароматические	17,00	11,28—15,85
13 средние ароматические	14,20	23,67—27,41
14 тяжелые ароматические	14,40	3,92—6,71
15 смолы	1,97	1,80—2,88

*All oils obtained from commercial mixture of sulfur-containing petroleums (Tuymazy, Bavly, Bugul'ma and Mukhanovo).
**The values indicated are the extremes for DS-14 oils obtained by mixing various distillate and residual components [26].

1) Index
2) Oil
3) DS-8
4) Density
5) Kinematic viscosity, cSt
6) At
7) Viscosity index
8) Refractive index
9) Sulfur
10) Group chemical composition
11) Naphthenoparaffinic
12) Light aromatic
13) Medium aromatic
14) Heavy aromatic
15) Tars.

TABLE 6.39

Physicochemical Properties and Group Chemical Composition of Aviation Oils

1 Показатели	2 Масло				
	МК-20	3 МС-20			
	4 из сураханской отборной нефти	5 из смеси концентратов карачухуро-сураханских и грозненских нефтей	6 из карачухуро-сураханской нефти	7 из жирновской нефти	8 из смеси сернистых нефтей (туймазинской, бавлинской, бугульминской и мухановской)
9 Плотность ρ_4^{20}	0,9004	0,895	—	—	0,8990
10 Вязкость кинематическая, *сст*:					
11 при 50° C	—	161	—	—	159,4
» 100° C	23,1	20,8	—	—	21,6
12 Вязкостно-весовая константа	0,8285	0,8160	—	—	—
13 Индекс вязкости	78	82	—	—	85
14 Температура вспышки, °C					
15 в открытом тигле	—	270	—	—	—
16 в закрытом тигле	—	250	—	—	—
17 Температура застывания, °C	—	—19	—	—	—
18 Коксуемость, %	—	0,29	—	—	—
19 Стабильность по АзНИИ:					
20 индукционный период, *мин*	24	—	—	—	—
21 общее время окисления, *мин*	226	—	—	—	—
22 Коррозия по Пинкевичу на свинцовых пластинках, *г/м²*	3,0	—	—	—	—
23 Сера, %	—	—	—	—	1,08
24 Групповой химический состав, %:					
25 нафтено-парафиновые	69,0	70,3	71,5	69,2	50,4
26 ароматические	25,0	27,1	27,0	29,0	45,4
27 смолы и [illegible]ри	6,0	2,6	4,5	1,8	4,2
28 Кольцевой состав, %					
29 нафтеновые кольца	25,0	—	—	—	—
30 ароматические кольца	2,4	—	—	—	—
31 парафиновые цепи	72,6	—	—	—	—

1) Index
2) Oil
3) MS-20
4) From Surakhany select petroleum
5) From mixed concentrates of Karachukhur-Surakhany and Groznyy petroleums
6) From Karachukhur-Surakhany petroleum
7) From Zhirnovsk petroleum
8) From mixed sulfur-containing petroleums (Tuymazy, Bavly, Bugul'ma and Mukhanovo)
9) Density
10) Kinematic viscosity, cSt
11) At
12) Viscosity-weight constant
13) Viscosity index
14) Flash point
15) Open crucible
16) Closed crucible
17) Pour point
18) Coking capacity
19) AzNII stability
20) Induction period, min
21) Total oxidation time, min
22) Pinkevich corrosion on lead plates, g/m²

23) Sulfur
24) Group chemical composition
25) Naphthenoparaffinic
26) Aromatic
27) Tars and losses
28) Ring composition
29) Naphthenic rings
30) Aromatic rings
31) Paraffinic chains.

9. DEPOSITS IN INTERNAL-COMBUSTION ENGINES

The carbon-containing deposits formed on the components of internal combustion engines are classified as scale, varnish and sludge.

Scale is composed of hard carbon-containing substances deposited on combustion-chamber walls, valves, sparkplugs, and on the top face and the upper part of the side of the piston.

Varnish deposits are thin varnish-like films formed on the piston in the piston-ring zone and on the skirt and inside walls of the pistons.

Sludge is a greasy coagulum that collects on crankcase walls, in crankshaft journals, on filters and in oil lines.

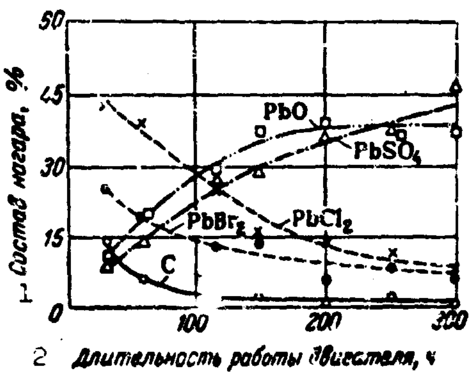


Fig. 6.15. Influence of engine running time on composition of scale formed in combustion chamber [28] (tests on gasoline containing 0.54 ml/kg of TEL). 1) Composition of scale, %; 2) engine running time, h.

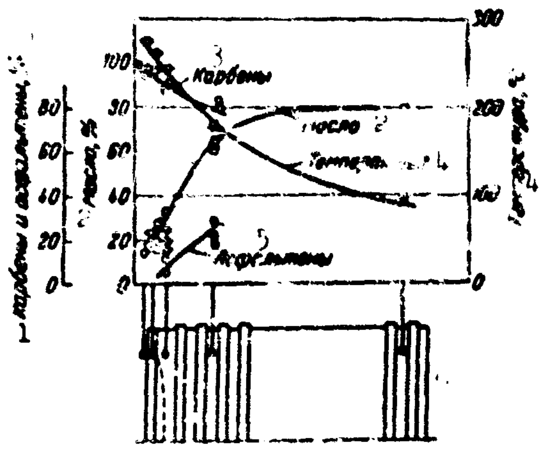


Fig. 6.16. Influence of piston temperature in 1MCh-10.5/13 engine on composition of carbon-bearing deposits [le]. 1) Carbenes and asphaltenes, %; 2) oil; 3) carbenes; 4) temperature; 5) asphaltenes.

TABLE 6.40

Elementary Composition of Scale on Piston Face in Aviation Engine [31]

1 Масло	2 Элементарный состав, %			
	C	H	O	3 зола
4 Дистиллятное вязкостью 18 сст при 100° С	71,9	4,8	19,6	3,7
5 Индустриальное 50	75,8	4,5	18,3	1,4

Note. Engine operated on unleaded gasoline; test time 100 hr.

1) Oil
2) Elementary composition, %
3) Ash
4) Distillate, viscosity 18 cSt at 100°C
5) Industrial 50.

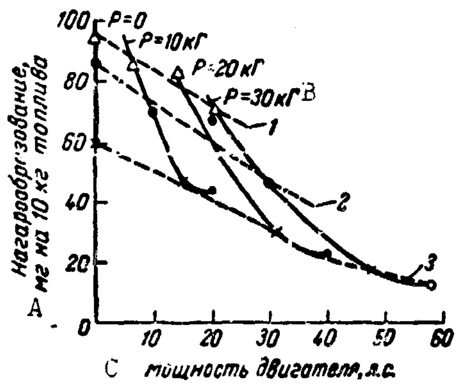


Fig. 6.17. Influence of speed, load and effective power of ZIL-120 engine on scale formation [29]: 1) 700 rev/min; 2) 1000 rev/min; 3) 1600 rev/min; o) 2000 rev/min. A) Scale buildup, mg to 10 kg of fuel; B) kg; C) engine power, hp.

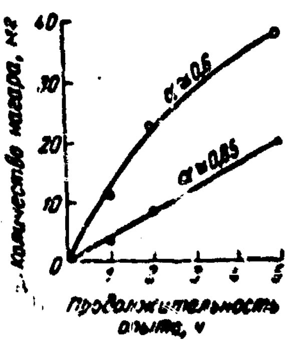


Fig. 6.18. Influence of fuel-mixture composition on scaling in ZIL-120 engine [29]. A) Amount of scale, mg; B) test time, h.

TABLE 6.41

Composition of Carbon Deposits in Two-Stroke, Gasoline-Fueled Vehicle Engine [32]

1 Место отбора углеродистых отложений	2 Масло, %	3 Смолы и окси-кислоты, %	4 Асфальтены, %	5 Кокс, %	6 Зола, %
7 Днище поршня	3,4	1,5	1,5	90,8	2,8
8 Головка цилиндра	6,6	2,1	2,8	86,1	2,4
9 Детали выпускной системы	21,7	1,1	3,2	69,3	4,7
10 Канавки поршня	38,9	4,8	3,3	44,0	9,0

Note. Test run under stand conditions on unleaded gasoline.

1) Carbon deposits taken from
2) Oil
3) Tars and hydroxy-acids
4) Asphaltenes
5) Coke
6) Ash
7) Top of piston
8) Cylinder head
9) Exhaust-system parts
10) Piston-ring grooves.

It is customary to characterize carbon deposits on the basis of their elementary composition and their contents of tars, asphaltenes, carbenes, carboids, ash and other products. The compositions of the deposits and sludges (Tables 6.40-6.47, Figs. 6.15, 6.16) and their rates of formation (Tables 6.48, 6.49 and Figs. 6.17, 6.19) depend on the design features of the engine, running speed, operating conditions, and the quality of the fuel and oil used.

As the temperature of the engine parts rises and it continues to run, the content of volatile compounds in the deposits decreases (Figs. 6.15, 6.16). Running an engine on fuel containing TEL tends to increase the amount of noncombustible products in the scale (see Tables 6.41 and 6.42).

The speed, load and power of the engine and the composition of the fuel mixture (see Figs. 6.17, 6.18) have considerable influence on the rate of scale formation. This rate is also observed to rise when the fuel contains more tetraethyllead and sulfur.

Formation of varnish deposits depends directly on the content of sulfur compounds in the fuel; in addition, the rate of varnish formation is determined by the group chemical composition of the oil (see Tables 6.48 and 6.49 and Fig. 6.19) and the effectiveness of additives used in it.

Carbon-containing deposits cause many kinds of trouble in operating internal-combustion engines: buildup of scale results in coking of spark plugs, interference with valve operation and the combustion process, and a drop in engine power output (Fig. 6.20); as a result, the engine comes to require fuel with a higher octane

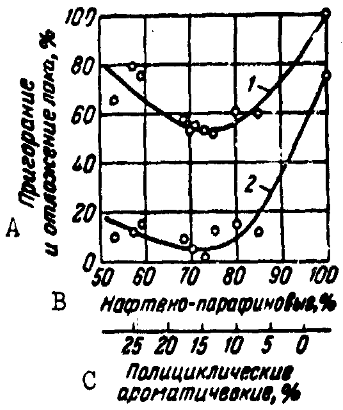


Fig. 6.19. Operational properties of MS-20 oil from Karachukhur-Surakhany raw material as functions of hydrocarbon composition [30] (test on 2Ch-8.5/11 engine): 1) formation of varnish deposits on piston skirt; 2) scorching of piston rings. A) Scorching and deposition of varnish, %; B) naphthenoparaffinic, %; C) polycyclic aromatic, %.

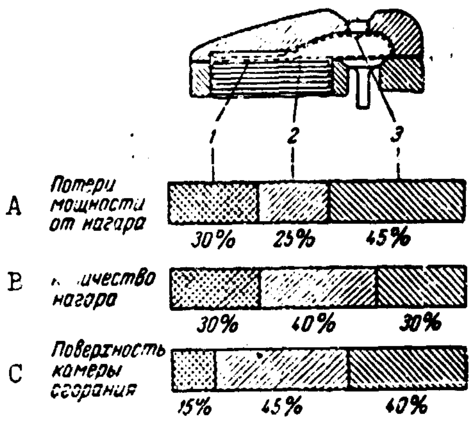


Fig. 6.20. Influence of location of scale in combustion chamber on engine power losses due to scaling: 1) cooled part of head; 2) top of piston, valve; 3) part of head vigorously rinsed by fuel mixture entering cylinder. A) Power losses due to scale; B) amount of scale; C) combustion chamber surface.

TABLE 6.42

Composition of Carbon-Containing Deposits on Components of Single-Cylinder Engine Operating on Leaded Gasoline [33]

1 Место отбора углеродистых отложений	2 Общее содержание свинца в отложениях, %	3 Содержание соединений свинца в отложениях, %			7 Прочие примеси, %
		4 галоидный свинец	5 окисный свинец	6 металлический свинец	
8 Днище поршня	60.22	45.28	14.89	12,76	27,09
9 Головка цилиндра	69.36	60.20	16.66	9,01	14,13
10 Головка выпускного клапана	85.60	4.20	88.40	0,0	7,80
11 Свечи	81.50	38.20	51.10	5,62	5,08

1) Carbon deposits taken from
2) Total lead content in deposits
3) Content of lead compounds in deposits
4) Lead halide
5) Lead oxide
6) Metallic lead
7) Other impurities
8) Top of piston
9) Cylinder head
10) Exhaust-valve head
11) Plug.

TABLE 6.43

Composition of Lead Deposits on Various Engine Parts (Averages) [34]

1 Соединение свинца	2 Температура плавления, °C	3 Детали двигателя, на которых образовались отложения				
		4 камера сгорания	5 днище поршня	6 впускной клапан	7 изолятор свечи	8 выпускной клапан
$PbBr_2$	370	+	+	—	+	—
$2Pb \cdot PbBr_2$	710	+	+	+	—	+
$2PbO \cdot 3PbBr_2$	438—540	—	—	—	+	—
$3PbO \cdot PbBr_2$	710	—	—	—	+	—
PbO	888	—	—	—	—	+
$PbO \cdot PbSO_4$	980	—	—	—	+	+
$2PbO \cdot PbSO_4$	960	—	—	—	—	+
$4PbO \cdot PbSO_4$	900—920	—	—	—	—	+

Note. Engine operated on leaded gasoline containing sulfur.

1) Lead compound
2) Melting point
3) Engine parts on which deposits were formed
4) Combustion chamber
5) Piston head
6) Intake valve
7) Plug insulator
8) Exhaust valve.

TABLE 6.44

Composition of Varnish Deposits on Parts of Aviation Engine [31]

1 Масло	2 Детали, с которых сняты лаковые отложения	3 Состав отложений, %				8 Элементарный состав отложений, %			
		4 масло и нейтральные смолы	5 асфальтены	6 карбены и карбоиды	7 зола	C	H	O	7 зола
9 Дистиллятное вязкостью 18 *сст* при 100° C	10 Юбка поршня	39,8	8,5	49,9	1,8	82,[illegible]	7,3	8,0	2,0
	11 Верхняя головка шатуна	37,1	9,4	51,0	2,4	81,3	7,0	9,1	2,5
12 Индустриальное 50	10 Юбка поршня	49,6	6,5	43,0	0,8	84,7	[illegible]	6,2	0,4
	11 Верхняя головка шатуна	48,6	6,9	43,4	1,1	84,8	8,0	6,1	1,7

Note. Engine run on unleaded gasoline; test time 100 h.

1) Oil
2) Parts from which varnish deposits were taken
3) Composition of deposits
4) Oil and neutral tars
5) Asphaltenes
6) Carbenes and carboids
7) Ash
8) Elementary composition of deposits, %
9) Distillate, with viscosity of 18 cSt at 100°C
10) Piston skirt
11) Connecting rod upper end
12) Industrial 50.

rating. Varnish deposits tend to promote scorching of piston rings; in addition, formation of sludge tends to clog oil lines and pickup screens, and this, in turn, causes bearings to burn out (Tables 6.50, 6.51, 6.52). It is therefore necessary to prevent formation of carbon deposits in internal-combustion engines and to remove them periodically from engine parts. Table 6.53 gives recipes for washing solutions used to remove deposits from engine oil systems. The results of using these solutions are given in Table 6.54. Table 6.55 gives the compositions of solutions used to remove varnish and scale from engine parts after disassembly.

TABLE 6.45

Composition of Carbon-Containing Deposits on Parts of YaAZ-204 Engine [35]

1 Детали двигателя	2 Состав отложений, %					8 Элементарный состав отложений, %			
	3 масло и смолы	4 оксикислоты	5 асфальтены	6 карбены и карбоиды	7 зола	C	H	O	9 несгораемый остаток
10 Головка цилиндров	29,43	2,03	0,54	63,94	4,06	73,96	4,78	16,47	4,79
11 Поршень:									
12 днище	19,12	2,53	0,54	69,68	8,13	70,00	3,55	17,62	8,83
13 головка выше 1-го кольца	15,22	4,79	1,00	74,47	4,52	71,96	3,77	19,62	4,65
14 канавка 1-го кольца	12,30	11,66	0,80	73,15	2,09	73,58	3,51	20,36	2,55
канавка 2-го кольца	13,32	8,03	1,29	74,95	2,41	77,10	4,31	17,07	1,52
канавка 3-го кольца	13,25	11,25	1,22	70,65	3,63	75,36	4,10	17,01	3,53
канавка 4-го кольца	15,13	13,48	1,13	65,00	5,26	73,62	4,27	17,04	5,07
15 канавки 5-го и 6-го колец	37,78	7,72	0,83	43,86	9,81	—	—	—	—
16 канавки 7-го и 8-го колец	36,59	10,33	1,52	39,79	11,77	—	—	—	—
17 Поршневые кольца:									
18 1-е компрессионное	12,24	13,02	0,44	71,53	2,77	—	—	—	—
2-е компрессионное	11,88	7,53	1,60	75,29	3,70	75,62	4,26	16,54	3,58
3-е компрессионное	18,39	13,06	2,72	61,68	4,15	—	—	—	—
4-е компрессионное	19.08	15.14	1.41	56,35	8.02	—	—	—	—
19 5-е и 6-е маслосъемные	35,53	9,82	0,60	41,04	13,01	—	—	—	—
20 7-е и 8-е маслосъемные	52,00	5,13	3,37	29,25	10,25	75,63	4,15	9,51	10,71
21 Гильза цилиндров: верхний пояс	30,00	4,24	1,18	63,33	1,25	75,84	4,63	18,34	1,19
22 Продувочные окна:									
23 1-я гильза	40,24	2,24	1,13	49,79	6,60	80,59	6,47	7,60	5,34
2-я гильза	34,68	1,78	1,12	57,06	5,16	80,65	5,62	9,03	4,70
3-я гильза	35,56	2,99	1,22	54,50	5,73	81,24	5,87	8,76	4,13
4-я гильза	40,40	1,76	1,17	51,84	4,83	82,31	5,66	7,95	4,08
24 клапаны	26,30	1,13	3,57	57,76	11,24	—	—	—	—

Note. Test run on oil with ЦИАТИМ-339 additive; test time 500 h.

1) Engine part
2) Composition of deposits, %
3) Oil and tars
4) Hydroxyacids
5) Asphaltenes
6) Carbenes and carboids
7) Ash
8) Elementary composition of deposits, %
9) Noncombustible residue
10) Cylinder head
11) Piston
12) Top
13) Side above 1st ring
14) Groove of ...th ring
15) Grooves for 5th and 6th rings
16) Grooves for 7th and 8th rings
17) Piston rings
18) ...th compression
19) 5th and 6th oil-control
20) 7th and 8th oil-control
21) Upper zone of cylinder sleeve
22) Ports
23) ...th sleeve
24) Valves.

TABLE 6.46

Elementary Composition of Carbon Deposits on Final Oil Filters of GAZ-51 Engine [36]

1 Масло	2 Элементарный состав, %		
	C	H	O
3 Индустриальное 50	78,5	11,5	10,0
4 АС-5	73,0	10,0	17,0

1) Oil
2) Elementary composition
3) Industrial 50
4) AS-5.

TABLE 6.47

Composition of Deposits in Engines of "Pobeda" and "Moskvich" Automobiles [31]

1 Автомобиль	2 Место отбора осадка	3 Состав осадка, %					
		4 вода	5 масло и смолы	6 оксикислоты	7 асфальтены	8 карбены, карбоиды	9 зола
10 «Победа»	11 Поддон картера	2,9	68,1	13,0	0,2	10,1	5.7
	Клапанная коробка 12	2,0	70,5	12,9	0,2	11,1	3,3
	Отстойник фильтра грубой очистки 13	1,0	73,3	10,6	0,8	9,6	4,7
	Сетка приемника маслонасоса 14	6,4	59,4	15,5	0,5	18,2	
	Коробка шестерен 15	5,6	57,5	17,7	0,3	18,9	
16 «Москвич»	Поддон картера	26,9	67,5	2,1	0,1	2,1	1,3
	Фильтр тонкой очистки 17	5,0	55,6	13,2	1,1	15,1	

Note. In view of the insignificant fuel content in the deposits, it was not included in the calculations.

1) Automobile
2) Deposits taken from
3) Composition of deposits
4) Water
5) Oil and tars
6) Hydroxyacids
7) Asphaltenes
8) Carbenes, carboids
9) Ash
10) "Pobeda"
11) Bottom of crankcase
12) Valve chamber
13) First-filter trap
14) Oil pump pickup screen
15) Timing case
16) "Moskvich"
17) Final filter.

TABLE 6.48

Influence of Group Chemical Composition of Oil on Formation of Carbon-Containing Deposits on Piston [37]

1 Продукты	2 Продолжительность работы, ч	3 Количество отложений на поршне и кольцах, г
4 Масло индустриальное 50	10 20 30 40 50	3,5 7,1 11,2 15,4 19,3
5 Нафтено-парафиновые углеводороды масла индустриального 50	6 16 26 36	4,5 11,8 19,1 27,1
6 Малоциклические ароматические углеводороды масла индустриального 50	10 20 30 40 50	3,2 6,3 9,1 12,3 15,5
7 Полициклические ароматические углеводороды масла индустриального 50	10 20 30 40	2,2 4,1 6,3 8,3
8 Масло АС-10,5 из сернистых нефтей	10 20 30 40	1,8 3,8 6,0 8,4
9 Нафтено-парафиновые углеводороды масла АС-10,5	10 20 30	2,7 6,0 11,1
10 Ароматические углеводороды масла АС-10,5	10 20 30 40	1,8 3,7 5,9 7,7

Note. Tests run on IT9-2 engine.

1) Product
2) Running time, h
3) Amount of deposits on piston and rings, g
4) Industrial oil 50
5) Naphthenoparaffinic hydrocarbons of industrial oil 50
6) Oligocyclic aromatic hydrocarbons of industrial oil 50
7) Polycyclic aromatic hydrocarbons of industrial oil 50
8) AS-10.5 oil from sulfur-containing petroleums
9) Naphthenoparaffinic hydrocarbons of AS-10.5 oil
10) Aromatic hydrocarbons of AS-10.5 oil.

TABLE 6.49

Influence of Group Chemical Composition of Oil on Formation of Varnish Deposits [38]

1 Продукты	2 Лакообразование на поршне установки ПЗВ, баллы
3 Масло МС-20 из карачухуро-сураханской нефти	3,5—4,0
4 Нафтено-парафиновая фракция масла МС-20	5,0—5,5
5 То же + ароматические углеводороды масла МС-20:	
6 15% моноциклических . .	5,0—5,5
25% » . .	5,0
40% » . .	5,0
7 5% полициклических . .	4,5—5,0
10% » . .	3,5—4,0
15% » . .	2,5—3,0

1) Product
2) Varnish formed on piston of PZV machine, points
3) MS-20 oil from Karachukhur-Surakhany petroleum
4) Naphthenoparaffinic fraction of MS-20 oil
5) Same + aromatic hydrocarbons from MS-20 oil
6) 15% monocyclic
7) 5% polycyclic.

TABLE 6.50

Influence of Engine Oil Change Interval on Formation of Deposits [39]

1 Неисправность	2 Количество автомобилей (в %), у которых наблю[illegible]сь неполадки при сроке смены масла		
	4000 км	6000 км	9500 км
3 Сетка маслоприемника забита осадками более чем на 30%	8	14	40
4 Маслопроводы полностью забиты осадками	8	28	60

Note. Engines showing little wear were selected for the tests; the vehicles were driven 50,000 km during the tests.

1) Complaint
2) Number of vehicles (in %) in which trouble was reported with oil change interval of
3) Oil pickup screen more than 30% blocked by deposits
4) Oil lines completely clogged by deposits.

TABLE 6.51

Fouling of Oil Pickup Screen by Deposits as Function of Vehicle Mileage

1 Пробег автомобиля, км	2 Степень загрязнения сетки маслоприемника осадками, %	3 Толщина отложений на сетке маслоприемника, мм
6000—7000	0—10	<1
12000—15000	20—50	<1
30000—40000	80—100	≤1
4 Свыше 40000	100	>1

1) Distance traveled by vehicle, km
2) Extent of oil pickup screen fouling by deposits, %
3) Thickness of deposits on oil pickup screen, mm
4) Above.

Note. The vehicles were operated under city driving conditions with an oil-change interval of 1600-2000 km.

TABLE 6.52

Influence of Deposit Formation on Engine Performance [12]

1 Неполадки в работе двигателей	2 Количество неполадок, %
3 Пригорание поршневых колец	67,3
4 Забивка маслопроводов	53,8
5 Выплавка подшипников	40,4
6 Пригорание клапанов	36,5

1) Engine trouble
2) Number of cases, %
3) Scorched piston rings
4) Oil line clogging
5) Bearings burned out
6) Valves burned.

TABLE 6.53

Composition of Washing Solutions Recommended for Removing Carbon Deposits from Engine Oil System [39]

1 Компоненты	2 Патент		
	№	3 год	4 страна
5 Керосино-газойлевый дистиллят + до 10% нафтената свинца, цинка или олова	2 160 911	1939	6 США
7 Легкое масло + 10% бензола, толуола или ксилола	2 279 001	1942	»
8 Веретенное масло + до 15% стеарата или лаурилсульфата натрия	2 403 169	1946	»

TABLE 6.53 (continued)

1 Компоненты	2 Патент №	3 год	4 страна
9 Смесь масла (50—75%) и лигроинового дистиллята (50—25%)	2 410 613	1946	6 США
10 Лигроино-керосиновый дистиллят + 1—20% присадки, полученной на базе пятисернистого фосфора	461 503	1949	11 Канада
12 Смесь фракции высококипящих углеводородов, содержащей не менее 50% ароматических углеводородов и 2—20% этиленгликолевого эфира	69 207	1952	13 Голландия
14 Моторное масло (50—75%) + смесь крезола и мыла (50—25%), состоящая из равных частей ортокрезола и раствора калиевого мыла, pH которого равно 8,5—9,0	2 671 036	1954	6 США
15 Смесь, состоящая из низших алкилзамещенных бензола с 7—10 углеродными атомами в молекуле (25—75%), монометилгликолевого эфира (75—25%) и эфира рицинолевой кислоты (0,1—10%)	2 672 450	1954	»
16 Смесь алкиламина, имеющего менее 9 углеродных атомов (10—25%), моноалкильного гликолевого эфира (20—40%), хлорированного бензола, содержащего 2—6 атомов хлора (15—35%), и ароматического углерода (10—50%)	729 329	1955	17 Англия

1) Components
2) Patent
3) Year
4) Country
5) Kerosene-gas-oil distillate + up to 10% naphthenate of lead, zinc or tin
6) USA
7) Light oil + 10% benzene, toluene or xylene
8) Spindle oil + up to 15% of sodium stearate or lauryl sulfate
9) Mixture of oil (50-75%) and ligroin distillate (50-25%)
10) Ligroin-kerosene distillate + 1-20% of additive prepared from phosphorus pentasulfide
11) Canada
12) Mixture of fraction of high-boiling hydrocarbons containing no less than 50% aromatics and 2-20% ethylene glycol ester
13) The Netherlands
14) Motor oil (50-75%) + mixture of cresol and soap (50-25%) consisting of equal parts of orthocresol and solution of potassium soap with pH of 8.5-9.0
15) Mixture consisting of lower alkyl-substituted benzenes with 7-10 carbons in the molecule (25-75%), glycol monomethyl ester (75-25%) and ricinoleic acid ester (0.1-10%)
16) Mixture of an alkylamine with fewer than 9 carbons (10-25%), a monoalkyl glycol ester (20-40%), chlorinated benzene containing 2-6 chlorine atoms (15-35%) and aromatic carbon [sic] (10-50%)
17) England.

TABLE 6.54

Influence of Washing Solution in Raising Engine Compression [12]

1 № цилиндра	2 Компрессия, кГ/см²		5 Изменение компрессии, кГ/см²	1 № цилиндра	2 Компрессия, кГ/см²		5 Изменение компрессии, кГ/см²
	3 до промывки	4 после промывки			3 до промывки	4 после промывки	
6 Грузовой автомобиль (пробег 92 500 км)				7 Легковой автомобиль (пробег 41 750 км)			
1	6,9	7,4	+0,5	1	6,0	8,0	+2,0
2	7,0	7,6	+0,6	2	6,3	8,3	+2,0
3	6,9	7,0	+0,1	3	7,0	8,0	+1,0
4	3,9	7,4	+3,5	4	6,7	8,0	+1,3
5	6,0	7,3	+1,3	5	4,9	7,7	+2,8
6	6,3	7,0	+0,7	6	6,3	8,3	+2,0
				7	7,0	8,0	+1,0
				8	5,3	8,0	+1,7

1) Cylinder No.
2) Compression, kg/cm²
3) Before washing
4) After washing
5) Compression change, kg/cm²
6) Truck (mileage 92,500 km)
7) Passenger car (mileage 41,750 km).

TABLE 6.55

Composition of Solutions for Removal of Varnish Deposits and Scale from Engine Parts [31]

1 Компоненты	2 Количество воды, г/л	
	3 для очистки стальных и чугунных деталей	4 для очистки алюминиевых деталей
5 Едкий натр	25	—
6 Сода	33	18,5
7 Зеленое мыло	8,5	10
8 Жидкое стекло	—	8,5

Note. The parts are kept in the solution for 2-3 hr at 85-90°C, washed with water and then brushed clean.

1) Component
2) Amount of water, g/liter
3) For cleaning steel and cast iron parts
4) For cleaning aluminum parts
5) Caustic soda
6) Soda
7) Green soap
8) Water glass.

10. OIL CONSUMPTION IN ENGINES

Oil consumption in an engine is determined by its operating regime, design features and general condition, as well as by the quality of the lubricating oil. It is composed of the amount of oil originally put into the engine and the amounts added periodically to replace oil burned, evaporated and lost through clearances and seals.

The approximate per-hour consumption of crankcase oil can be calculated by the formula

$$Q_{ch} = \frac{q \cdot N \cdot K}{1000} + \frac{Q_z}{T_p}$$

where Q_{ch} is the rate of oil consumption in kg/h;

q is the specific oil consumption recommended by the engine manufacturer in g/(hp-h);

N is the engine's rated power, hp;

K is a coefficient that takes account of cylinder and bearing wear and is equal to:

1.25-1.30 for high-speed engines (>500 rev/min) when the bearings are pressure-lubricated and the cylinders are lubricated by splash;

1.2 for slow engines (200-500 rev/min) with the same lubricating-system design;

1.1 for slow engines with lubricator lubrication;

1.05 for slow engines with ring or chain lubrication of the main bearings, centrifugal lubrication of connecting-rod bearings, and lubricator lubrication of the cylinders;

Q_z is the oil filling of the crankcase in kg;

T_r is the working time of the oil in hours.

In automotive engines, oil consumption is usually calculated in per cent of fuel consumption, and amounts to about 3.5% for new engines that have not had a major overhaul and from 4 to 6% depending on degree of wear for all others.

For engines with compression ignition (stationary, marine, locomotive), the following approximate consumption norms, which have been developed on the basis of manufacturers' data and generalization of operating experience [5], may be adopted:

1. Two-stroke semidiesel engines:

a) compression ratio below 6

engine power, hp	10-25	25-75
oil consumption, g/(hp-h)	30-20	20-15

b) compression ratio 6-8.5

engine power, hp	below 40
oil consumption, g/(hp-h)	15-20

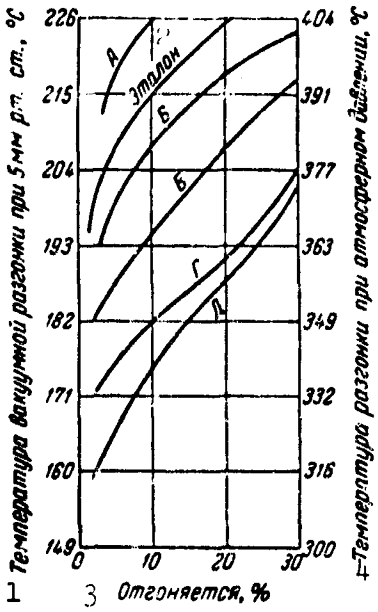


Fig. 6.21. Influence of fractional composition of oil on oil consumption (tests of a number of oils with 6.8-cSt viscosity on Lawson engine at 100°C) [12].

Масло 5	6 Коэффициент расхода
А	1,0; 0,95; 1,0; 1,05
2 Эталон	1,0
Б	1,05; 1,0; 1,0; 0,95
В	1,2; 1,1; 1,2
Г	2,0; 1,9; 1,8; 1,9
Д	2,3; 2,5

1) Vacuum-distillation temperature at 5 mm Hg, °C; 2) standard; 3) distilled over, %; 4) distillation temperature at atmospheric pressure, °C; 5) oil; 6) consumption coefficient.

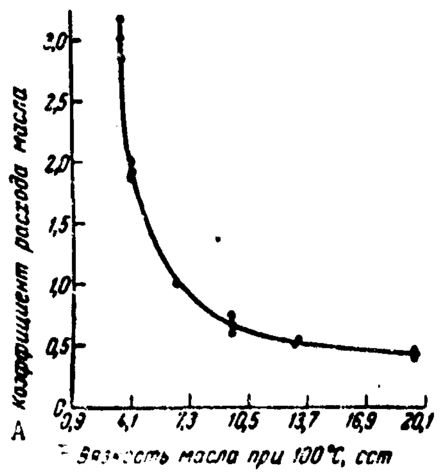


Fig. 6.22. Influence of oil viscosity on oil consumption in Lawson single-cylinder engine [12]. A) Oil consumption coefficient; B) viscosity of oil at 100°C, cSt.

2. Four-cycle high-compression petroleum engines:

engine power, hp................	below 40
oil consumption, g/(hp-h).......	12-10

3. Unsupercharged diesels:

a) two-stroke

engine power in one cylinder, hp	50-100	100-150
oil consumption, g/(hp-h).......	22-18	18-12

b) four-stroke

engine power in one cylinder, hp......	below 50	50-100	100-150
oil consumption, g/(hp-h)..........	10-8	8-6	6-4

4. Four-cycle supercharged diesels:

engine power in one cylinder, hp......	below 50	50-100	100-150
oil consumption, g/(hp-h)..........	8-6	7-6	6-4

The norms given above apply for oils with certain average properties - fractional composition and viscosity. In the general case, the higher the content of low-boiling fractions in the oil, the larger will be the amount burned and vaporized off, and this will make up the major part of oil consumption (Fig. 6.21).

A definite relationship is also observed between oil consumption and oil viscosity: consumption decreases with increasing viscosity (Fig. 6.22).

REFERENCES

1. Boltinskiy, V.N., Avtotraktornyye dvigateli [Auto-Tractor Engines], Sel'khozizdat, 1958.

2. Papok, K.K., Ragozin, N.A., Tekhnicheskiy slovar'-spravochnik po toplivu i maslam [Technical Reference Dictionary for Fuels and Oils], Gostoptekhizdat, 1963.

3. Blagovidov, I.F., Puchkov, N.G. et al., Khimiya i tekhnologiya topliv i masel, No. 2 (1963).

4. Yershov, N.V., Khimiya i tekhnologiya topliv i masel, No. 10 (1964).

5. Streets, R.E., The Engine Testing of Crankcase Lubricating Oils, Institute of Petroleum, London, 1962, page 161.

6. Les huiles pour moteurs et le graissage des moteurs [Motor Oils and Motor Lubrication], Vols. I, II, Technip, Paris, 1962.

7. Vipper, A.B., Vilenkin, A.V., Khimiya i tekhnologiya topliv i masel, No. 1 (1965).

8. Firsanova, Ye.N., in collection "Prisadki k maslam i toplivam" [Additives for Oils and Fuels], Gostoptekhizdat, 1961.

9. Bondi, A., Physical Chemistry of Lubricating Oils, New York, 1951.

10. Semenido, Ye.G., in collection "Povysheniye kachestva i primeneniye smazochnykh materialov" [Improving the Quality and Utility of Lubricating Materials], edited by B.V. Losikov, S.E. Kreyn and G.I. Fuks, Gostoptekhizdat, 1957.

11. Volarovich, M.P., Nizkotemperaturnyye svoystva masel [Low-Temperature Properties of Oils], Izd. AN SSSR, 1947.

12. Dzhordzhi, K.V., Motornyye masla i smazka dvigatelya [Motor Oils and Engine Lubrication] (translated from the English), Gostoptekhizdat, 1960.

13. Losikov, B.V., Puchkov, N.G., Englin, B.A., Osnovy primeneniya nefteproduktov [Fundamentals of the Application of Petroleum Products], Gostoptekhizdat, 1959.

14. Puchkov, N.G., Rubinshteyn, S.F., in collection "Issledovaniye i primeneniye nefteproduktov" [Petroleum Products Research and Applications], No. 6, Gostoptekhizdat, 1957.

15. Puchkov, N.G., Borovaya, M.S., Khimiya i tekhnologiya topliv i masel, No. 4 (1958).

16. Losikov, B.V., Lukashevich, I.P., Neftyanoye tovarovedeniye [Petroleum Commerce], Gostoptekhizdat, 1950.

17. Morozov, G.A., Primeneniye dizel'nykh masel s prisadkami [Use of Diesel Oils with Additives], Gostoptekhizdat, 1962.

18. Kreyn, S.E., Borovaya, M.S., in collection "Sostav i svoystva vysokomolekulyarnoy chasti nefti" [Composition and Properties of the Macromolecular Fraction of Petroleum], Izd. AN SSSR, 1958.

19. Druzhinina, A.V., Korotkov, P.N., Filippov, V.F., in collection "Khimiya sero- i azotorganicheskikh soyedineniy, soderzhashchikhsya v neftyakh i nefteproduktakh" [Chemistry of Sulfur- and Nitrogen-Organic Compounds Present in Petroleums and Petroleum Products], Vol. III, Izd. AN SSSR, 1960.

20. Demchenko, V.S., Novikov, V.K., in collection "Khimiya seroorganicheskikh soyedineniy, soderzhashchikhsya v neftyakh i nefteproduktakh" [Chemistry of Sulfur-Organic

Compounds Present in Petroleums and Petroleum Products], Vol. IV, Gostoptekhizdat, 1961.

21. Papok, K.K., Zarubin, A.P. et al., in collection "Prisadki k maslam i toplivam" [Additives for Oils and Fuels], Gostoptekhizdat, 196_.

22. Kyuregyan, S.K., Kuznetsova, O.A., Khimiya i tekhnologiya topliv i masel, No. 2 (1959).

23. Papok, K.K., Zarubin, A.P., Zakharov, G.V., loc. cit.

24. Papok, K.K., Zuseva, B.S., Khimiya i tekhnologiya topliv i masel, No. 6 (1960).

25. Puchkov, N.G., Borovaya, M.S., Zelenskaya, R.G., Khimiya i tekhnologiya topliv i masel, No. 8 (1958).

26. Kreyn, S.E., Vipper, A.B., Kazanskiy, V.L., Badyshtova, K.M., Kleymenova, Z.A., Lisovskaya, M.A., Ivankina, E.B., in collection "Opyt proizvodstva i primeneniya prisadok k motornym maslam" [Experience in the Production and Use of Motor-Oil Additives], TsNIITEIneftegaz, 1963.

27. Kreyn, S.E., Badyshtova, K.M., Vipper, A.B., Ryazanov, L.S., Nepogod'yev, A.V., Yastrebov, G.I., loc. cit.

28. Dumont, L.F., SAE Quarterly Transactions, October, 1951.

29. Papok, K.K. Livshits, S.M., Khimiya i tekhnologiya topliv i masel, No. 12 (1960).

30. Kreyn, S.E., Yevdokimov, O.P., Trudy Tret'yey Vsesoyuznoy konferentsii po treniyu i iznosu v mashinakh [Transactions of Third All-Union Conference on Friction and Wear in Machines], Vol. III, Izd. AN SSSR, 1960.

31. Papok, K.K., Vipper, A.B., Nagary, lakovyye otlozheniya i osadki v avtomobil'nykh dvigatelyakh [Scale, Varnish Deposits, and Sludge in Automotive Engines], Mashgiz, 1956.

32. Bouman, S.A., Properties of Lubricating Oil and Engine Deposits, London, 1950.

33. Feygin, A.L., Bekhlin, Yu.G., Trudy TsIAM, No. 130, Oborongiz, 1947.

34. Erdöl u. Kohle, No. 2, 78 (1954).

35. Traktovenko, I.A., Khimiya i tekhnologiya topliv i masel, No. 11 (1959).

36. Puchkov, N.G., Borovaya, M.S., Zelenskaya, R.G., Belyanchikov, G.P., Khimiya i tekhnologiya topliv i masel, No. 2 (1959).

37. Tsiguro, T.A., Druzhinina, A.V., Filippov, V.F., Khimiya i tekhnologiya topliv i masel, No. 2 (1959).

38. Kreyn, S.E., in collection "Khimicheskiy sostav i ekspluatatsionnyye svoystva smazochnykh masel" [Chemical Composition and Operational Properties of Lubricating Oils], Gostoptekhizdat, 1957.

39. Perriguey, W.G., SAE Journal, October, 1949.

Manuscript Page No.	Transliterated Symbols
455	ч = ch = chasovoy = per hour
455	з = z = zalivayemyy = poured in
455	р = r = rabota = work, working, running